EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023

EURL-PT-POP_2301-MP

FOOD

Report

PBDEs and HBCDDs

(Report Version 1.0)

11 March 2024

EURL POPs

EURL for halogenated POPs in Feed and Food
c/o State Institute for Chemical and
Veterinary Analysis Freiburg

Bissierstraße 5
79114 Freiburg
D-Germany

contact@eurl-pops.eu
+49 761 8855 500

eurl-pops.eu

Summary

Test sample	**FOOD:** Milk Powder [2301-MP]
Analytes of interest **Mandatory** for NRLs:	**PBDEs** (BDE-28, -47, -49, -99, -100, -153, -154, -183, -209) **HBCDDs** (α-HBCDD, β-HBCDD, γ-HBCDD or total HBCDD)
Methods	Any kind of method
Participants	NRLs, OFLs, other official laboratories, commercial laboratories performing the analysis of samples taken by food business operators
Statistical evaluation	ISO 13528:2022 [1], IUPAC Protocol [2]
Report of final results	11 March 2024 (Version 1.0)
Publication	EURL POPs reserves all rights to publish and present the anonymised results of the interlaboratory study in scientific journals and/or during conferences.

1. Structure of the PT, test material and analytes

This proficiency test (PT) on the determination of **PCDD/Fs, PCBs, PBDEs, HBCDDs** and **PFASs** in **milk powder** was organized by the EURL for halogenated POPs in Feed and Food to be performed between February and April 2023. The objective was to assess analytical performance of laboratories and interlaboratory comparability of results from analyses of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in one sample of **milk powder**.

National Reference Laboratories (NRLs) for halogenated POPs in Feed and Food from EU member states were requested to participate as part of their work programme for 2023. NRLs were invited to encourage the participation of **Official Laboratories (OFLs)** from their member states as part of their duties following Article 101 of regulation (EU) 2017/625 of the European Parliament and of the Council of 15 March 2017. Furthermore, participation of OFLs allowed the extension of the data basis for calculation of assigned values and evaluation of results.

Other official laboratories and **commercial laboratories** performing the analysis of samples taken by food business operators were invited to participate in this proficiency test. The evaluated results were discussed by representatives of European Commission, NRLs and the EURL at the EURL/NRL workshop in May 2023 in Berlin, Germany.

1.1. Samples and coding

The test material was prepared from commercially available food and fortified with analytes of interest using analytical standards or technical mixtures of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs.

Milk powder	**Sample no. 2301-MP-xxx**

Each participant received about **90 g** of the test sample in a HDPE bottle.

1.2. Analytes of interest

Participants were requested to determine the following parameters:

Polybrominated diphenyl ethers (PBDEs)

- Individual congeners: BDE-28, -47, -49, -99, -100, -153, -154, -183, -209
- Sum of 8 PBDEs (without BDE-209)
- Sum of 9 PBDEs (with BDE-209)

Hexabromocyclododecanes (HBCDDs)

- α-HBCDD, β-HBCDD, γ-HBCDD stereoisomers
- Sum of α-, β-, γ-HBCDD (using HPLC methods)
- Total HBCDD (using GC methods)

1.3. Methods

All kinds of detection and quantification methods could be applied.

1.4. Coding of laboratories and confidentiality

The identity of participating laboratories will be kept confidential.
For NRLs of EU member states, the suggested "protocol for management of underperformance in comparative testing or lack of collaboration of National Reference Laboratories (NRLs)" will be followed. The confidentiality of NRLs will be kept according to this protocol.
For OFLs of EU member states cooperating with NRL, the respective NRLs will inform the EURL for halogenated POPs about the participating OFLs and will receive the respective laboratory codes, invoices for participation fee and certificates of participation of the OFLs.

1.5. Results of PBDEs and HBCDDs

Laboratories should:

- use their own reference standards for identification and quantification,
- report results for each analyte,
- report the limit of quantification (LOQ), at least for each non-quantified analyte,
- give method information and
- give information about the accreditation of the laboratory according to ISO/IEC 17025 *(for metrological traceability of consensus values of participants used as assigned values).*

Results had to be reported in **µg/kg wet weight (w. w.)** for PBDEs and HBCDDs.

2. Participating laboratories

This proficiency test was open for participation of:

- National Reference Laboratories (NRLs) of EU member states
- National Reference Laboratories of other European countries
- Official laboratories
- Commercial laboratories

129 laboratories registered for this proficiency test, of which 32 laboratories reported results for brominated contaminants (30 laboratories reported results for PBDEs and 20 laboratories reported results for HBCDDs).

Table 1: Participating laboratories

Participating laboratories	Region	No. of participants
National Reference Laboratories	European Union Other Countries	20 1
Official Laboratories	European Union Other European Countries Africa Americas Asia Oceania	8 - - - - 1
Commercial Laboratories	European Union Other European Countries Africa Americas Asia Oceania	2 - - - - -
	Total	32

2.1. Number of reported results

Table 2: Reported results for PBDEs and fat content for milk powder (2301-MP)

Reported results (2301-MP)	All laboratories	NRLs
BDE-28, -47, -99, -100, -153, -154, -183	30	19
BDE-49 / BDE-209	22 / 24	16 / 15
Sum of 8 PBDEs (without BDE-209) (ub)	27	16
Sum of 8 PBDEs (without BDE-209) (lb)	26	15
Sum of 9 PBDEs (with BDE-209) (ub)	21	12
Sum of 9 PBDEs (with BDE-209) (lb)	21	12
Lipid content	29	19

Table 3: Reported results for HBCDDs for milk powder (2301-MP)

Reported results (2301-MP)	All laboratories	NRLs
α-HBCDD	18	13
β-HBCDD	18	13
γ-HBCDD	18	13
Sum of α-, β-, γ-HBCDD (ub)	18	13
Sum of α-, β-, γ-HBCDD (lb)	18	13
Total HBCDD (using GC methods)	2	2

2.2. Accreditation

Table 4: Reported accreditation according to ISO/IEC 17025 by participants for PBDEs and HBCDDs

Milk powder	PBDEs	HBCDDs
Accreditation	23	9
No accreditation	6	10

2.3. Detection methods

The following detection methods were applied:

- GC-HRMS-, GC-MS/MS-methods for PBDEs
- GC-HRMS-, GC-MS/MS-, LC-MS/MS-, LC-HRMS-methods for HBCDDs

Table 5: Overview of chromatographic separation and detection methods for the determination of PBDEs and HBCDDs in milk powder (2301-MP)

Detection methods	PBDEs	HBCDDs
GC-HRMS	17	2
GC-MS/MS	11	-
GC-LRMS	2	-
LC-MS/MS	-	15
LC-HRMS	-	2

3. Test for sufficient homogeneity and stability

The test for sufficient homogeneity was performed according to ISO 13528:2022 [1] and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [2].

Therefore, 10 portions of the test samples 2301-MP were analysed in duplicate for PBDEs. The test for sufficient homogeneity was performed for the individual congeners and sum parameters. The test materials showed sufficient homogeneity for PBDEs for this proficiency test. The stability check of the analytes of interest applying room temperature storage was performed according to ISO 13528:2022 [1]. The test material showed sufficient stability for PBDEs for this proficiency test. Homogeneity and stability can be concluded also for HBCDDs due to similar physico-chemical properties for this proficiency test.

4. Determination of the assigned value

Statistical evaluation of the PT results was performed by the EURL for halogenated POPs in feed and food according to ISO 13528:2022 [1] and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories [2].

The determination of the assigned value was performed according [1] by estimating of the assigned value as the consensus of participants' results (using only results of physico-chemical methods). The Huber robust mean was taken as assigned value after excluding extreme outliers (outside the range of ± 50% of the median of all reported results) and examination of the distribution of the remaining results using histogram and Kernel density estimation, if necessary.

Assigned values were calculated for individual PBDE congeners, sum of 8 (without BDE-209) and sum of 9 (with BDE-209) PBDEs, for individual HBCDD diastereomers, sum of α-, β- and γ-HBCDD and total HBCDD (including limits of quantification (LOQs)), if possible. Additionally the median of all values was calculated.

For individual congeners (including LOQs) assigned values were only calculated according to the above mentioned procedure, if more than 2/3 of all results are above the LOQ and less than 1/3 of all results (including LOQs) are outside the range of ± 50 % of the median of all reported results. Levels for individual congeners are only taken for evaluation and calculation if these levels are equal to or above the LOQ; otherwise the LOQ will be taken instead.

Due to high variation of participants' results or limited number of value above the LOQ, no assigned values could be calculated for:

- (+/–)-γ- HBCDD, α-, β- and γ-HBCDD (lb), total HBCDD (using GC-methods)
- BDE-28, -49, -209

Since there are no traceable reference values available, the assigned values in this PT were calculated based on the Huber robust mean of the participants' results. Therefore, the assigned values are only traceable to the results of the participants. Additionally the results of all participants reporting results and the results of participants having accreditation according to ISO/IEC 17025 were compared for PBDE sum parameters and HBCDD individual stereoisomers and the sum of α-, β-, γ-HBCDD.
23 out of 30 participating laboratories reported to be accredited according to ISO/IEC 17025 for PBDEs and only 9 out of 20 for HBCDDs. No significant differences between the assigned values calculated for both data sets were observed (Table 6).

Table 6: Comparison of assigned values for all participants and participants with reported accreditation according to ISO/IEC 17025 for PBDE and HBCDD sum parameters

Sum parameters	Assigned value All participants	Assigned value ISO/IEC 17025 accreditation	Deviation
	µg/kg wet weight		%
Sum of PBDE without BDE-209 (ub)	0.652	0.661	<2
Sum of PBDE without BDE-209 (lb)	0.652	0.663	<2
Sum of PBDE including BDE-209 (ub)	0.856	0.858	<1
Sum of PBDE including BDE-209 (lb)	0.822	0.821	<1
α - HBCDD	0.162	0.166	2
β- HBCDD	0.0185	0.0191	3
Sum of α-, β-, γ-HBCDD (ub)	0.199	0.202	<2

4.1. PBDEs – individual congeners and sum parameter

The assigned values for the test sample 2301-MP were calculated as consensus of participants' results for individual PBDEs and sum parameters, taking into account the calculation criteria described above (Table 7 ; tabular summary see annex 1; Figure 1).

Table 7: Assigned values for PBDEs (rounded to three significant figures)

Milk powder (2301-MP)	Assigned value µg/kg (wet weight)
BDE-28	-
BDE-47	0.189
BDE-49	-
BDE-99	0.256
BDE-100	0.0528
BDE-153	0.0378
BDE-154	0.0228
BDE-183	0.0889
BDE-209	-
Sum of 8 PBDEs (without BDE-209) (ub)	0.652
Sum of 8 PBDEs (without BDE-209) (lb)	0.652
Sum of 9 PBDEs (with BDE-209) (ub)	0.856
Sum of 9 PBDEs (with BDE-209) (lb)	0.822

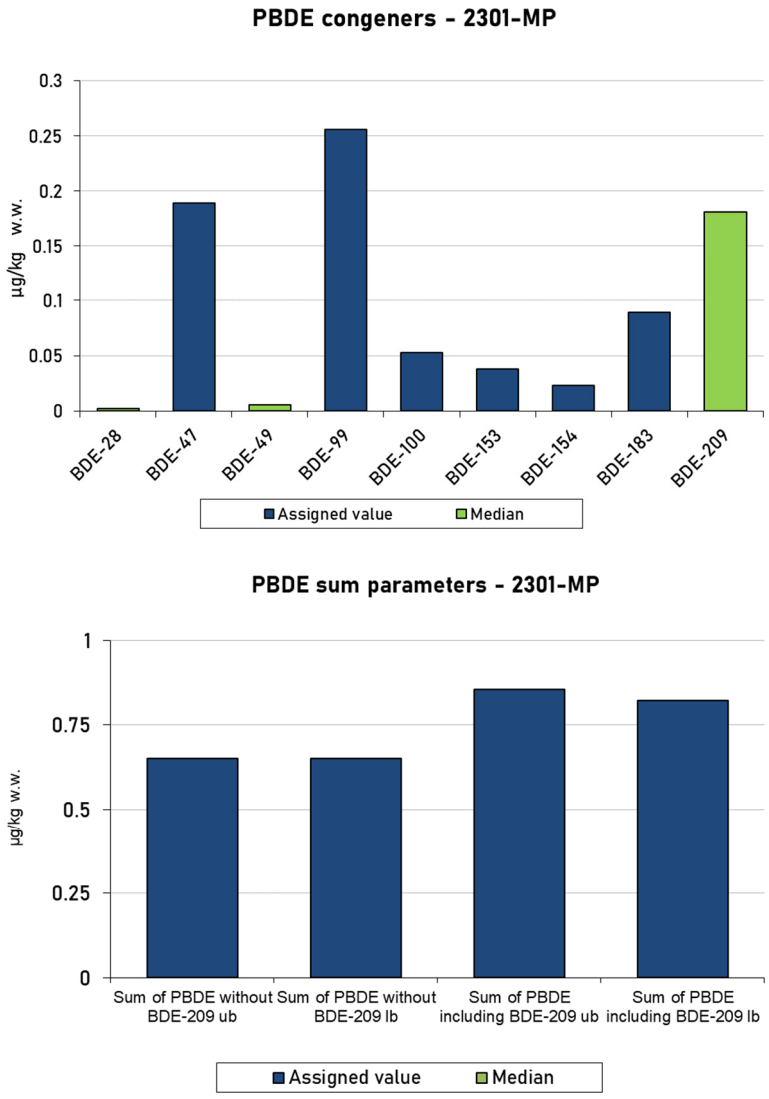


Figure 1: Assigned values (blue) and median values (green) for PBDE individual congeners and sum parameters for milk powder (2301-MP) [µg/kg wet weight]

4.2. HBCDDs – individual stereoisomers and sum parameter

The assigned values for the test sample 2301-MP were calculated as consensus of participants' results for individual HBCDDs and sum parameters, taking into account the calculation criteria described above (Table 8 ; tabular summary see annex 1; Figure 2).

Table 8: Assigned values for HBCDDs (rounded to three significant figures)

Milk powder (2301-MP)	Assigned value µg/kg (wet weight)
(+/–)-α- HBCDD	0.162
(+/–)-β- HBCDD	0.0185
Sum of α-, β-, γ-HBCDD (ub)	0.199

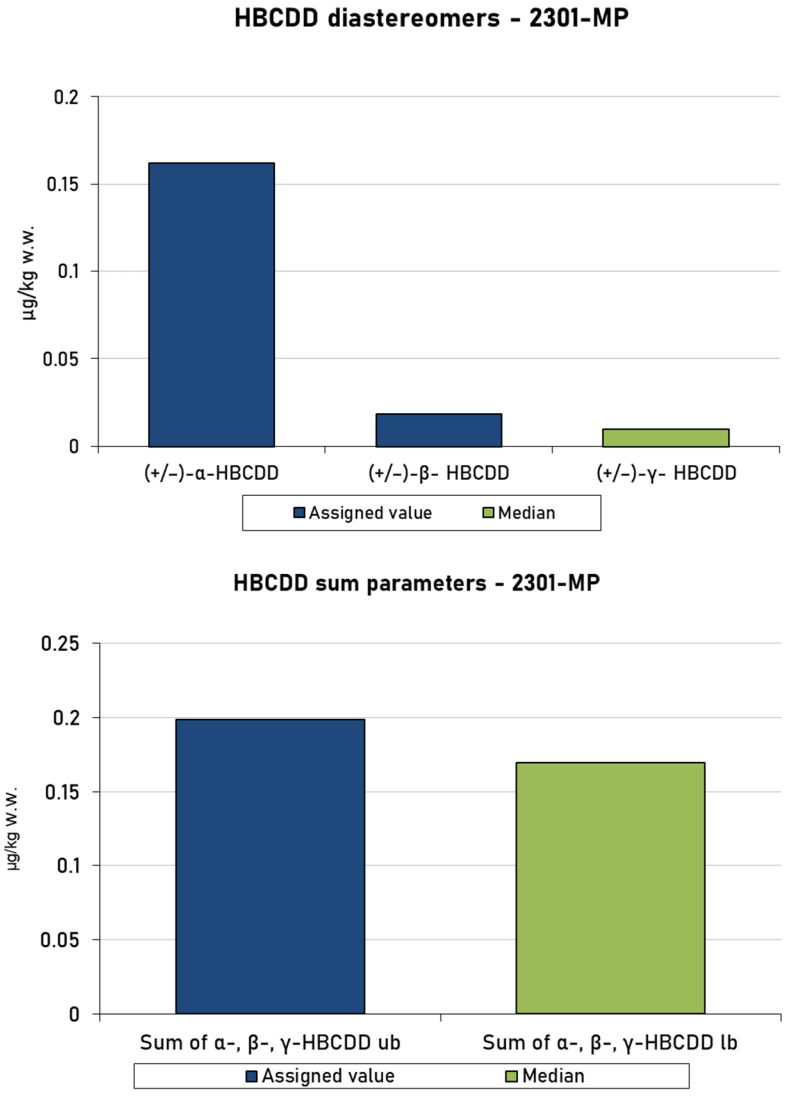


Figure 2: Assigned values (blue) and median values (green) for HBCDD individual congeners and sum parameters for milk powder (2301-MP) [µg/kg wet weight]

4.3. Lipid content

For the lipid content an assigned value of 9.02 % for the test sample 2301-MP was calculated as a consensus of the participants' results, taking into account the calculation criteria described above (tabular summary see annex 1).

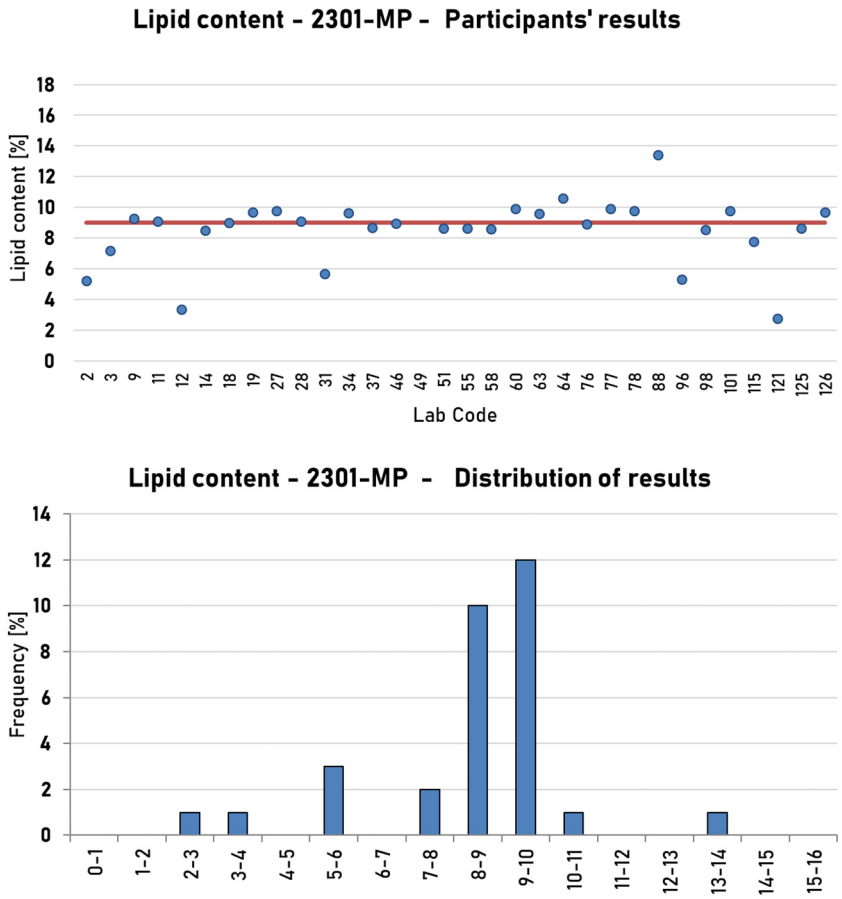


Figure 3: Participant's results (red line assigned value) and distribution of participant's results (blue bars) of the lipid content in % for milk powder (2301-MP)

4.4. Comparison of assigned values with recommended LOQs

The limits of quantification are currently based on the values specified in Commission Recommendation of 3 March 2014, on the monitoring of trace levels of brominated flame retardants in food (2014/118/EU). For PBDEs the recommended LOQ value is 0.01 µg/kg w.w. for individual congeners (Table 9). In the EURL "Guidance document on analytical parameters for the determination of organobromine contaminants in food and feed", a lower LOQ value of 0.001 µg/kg w.w. is targeted for all congeners except BDE-209, since some foods have concentrations below this value (Table 10; [3]). Valid data on the background contamination of

foodstuffs with BFRs is particularly important for a reliable risk assessment. For HBCDDs the recommended LOQ value is 0.01 µg/kg w.w. for α-, β- and γ-stereoisomers (Table 9). For total HBCDD measured by GC-MS, the corresponding LOQ value is 0.003 µg/kg (as cumulative response of all possible HBCDD diastereomers, Table 10).

Table 9: Recommended LOQs for PBDEs and HBCDDs from COMMISSION RECOMMENDATION of 3 March 2014 on the monitoring of traces of brominated flame retardants in food (2014/118/EU)

Food	Limit of quantification per congener/stereoisomer µg/kg (wet weight)
PBDEs	≤ 0.01
HBCDDs	0.01 ≤ 0.01

Table 10: Analytical recommendations from "Guidance document on analytical parameters for the determination of organobromine contaminants in food and feed" [3]

Food	Limit of quantification per congener/stereoisomer µg/kg (wet weight)
PBDEs	0.01 and 0.001 (all congeners except BDE-209)
HBCDDs	0.01 (sum of HBCDDs) and 0.003 (total HBCDD)

PBDEs:

All calculated assigned values were above the recommended LOQ of 0.01 µg/kg w.w. for the test sample milk powder (2301-MP). No assigned values could be calculated for BDE-28, -49 and -209. Therefore, the median values were used for comparison with the recommended LOQ of 0.01 µg/kg w.w. and the target LOQ of 0.001 µg/kg w.w, except for BDE-209 (Tables 9 and 10).

The median value for BDE-28 was 0.002 µg/kg, only 2 times higher than the target LOQ of 0.001 µg/kg. Although 22 out of 30 laboratories reported values above the LOQ for BDE-28, the variability of the participants' results according to the criteria described above (Chapter 4) was too large to calculate an assigned value.

For BDE-49 and BDE-209 the median values were 0.005 µg/kg and 0.181 µg/kg respectively, which is 5 times higher than the target LOQ of 0.001 µg/kg for BDE-49 and 18 times higher than the recommended LOQ of 0.01 µg/kg for BDE-209. No assigned values could be calculated for both congeners due to the high variability of the results obtained by the participants according to the criteria described above (Chapter 4).

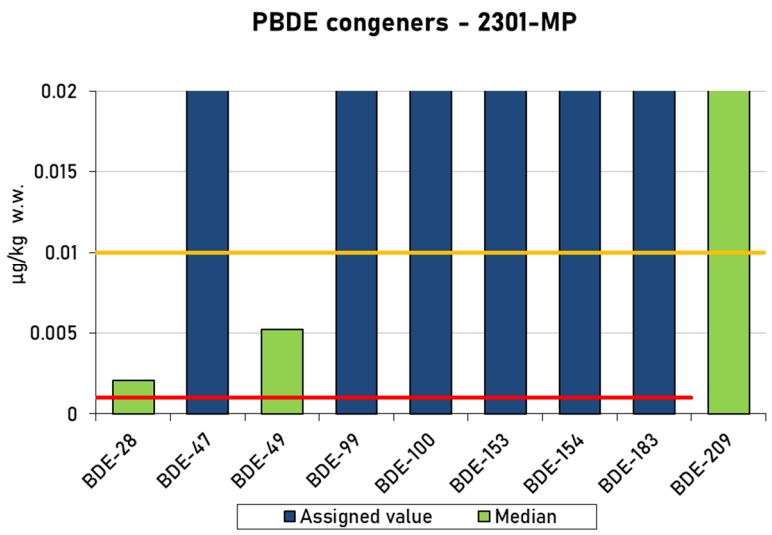


Figure 4: Comparison of assigned values for PBDE congeners with recommended LOQs (yellow line at 0.01 µg/kg wet weight and red line at 0.001 µg/kg wet weight) in milk powder (2301-MP)

HBCDDs:

For γ-HBCDD no assigned values could be calculated, because only 2 out of 18 laboratories reported results above the LOQ (see calculation criteria section 4). Therefore, the median values were taken for comparison with the recommended LOQs. The median value for γ-HBCDD was 0.01 µg/kg, which was in line with the recommended LOQ of 0.01 µg/kg wet weight (Tables 9 and 10), indicating that for the majority of laboratories the LOQs for γ-HBCDD were within the recommended LOQ range.

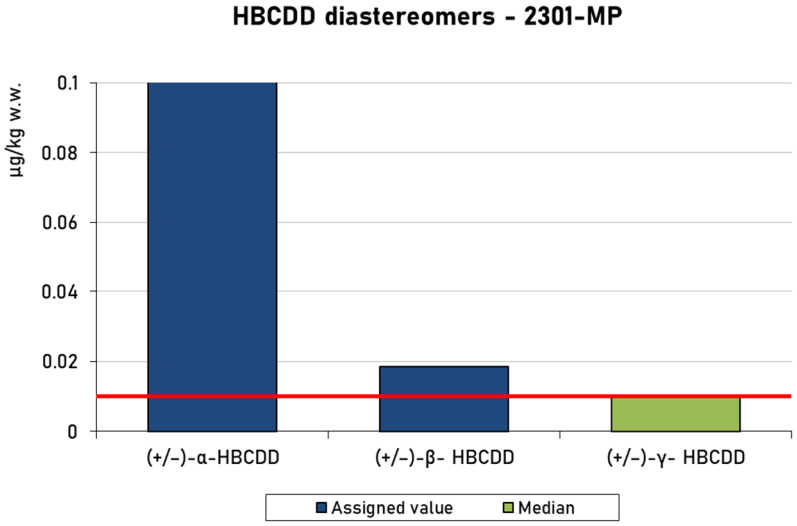


Figure 5: Comparison of assigned values for HBCDD stereoisomers with recommended LOQs (red line at 0.01 µg/kg wet weight) in milk powder (2301-MP)

5. Evaluation of results

5.1. Z-scores calculation

Criteria for successful participation of laboratories were based on the evaluation of the results of individual congeners and sum parameters. For evaluation of results of physico-chemical methods the z-scores were calculated according to the following formula:

$$z = \frac{(x - x_a)}{\sigma_p}$$

x: *participant's result*

x_a: *assigned value*

σ_p: *fitness-for-purpose-based standard deviation for proficiency assessment*

For individual PBDE congeners, individual HBCDD diastereomers and PBDE and HBCDD sum parameters, the standard deviation for proficiency assessment σ_p is defined as 20 %.

Z-scores for individual congeners / substances and diastereomers are only calculated and reported if levels for these congeners are equal to or above the LOQ. Otherwise, no z-scores will be given.

Interpretation of z-scores:

$\lvert z\text{-score} \rvert \leq 2$	*satisfactory performance*
$2 < \lvert z\text{-score} \rvert < 3$	*questionable performance (warning signal)*
$\lvert z\text{-score} \rvert \geq 3$	*unsatisfactory performance (action signal)*

5.2. PBDEs - Participants' z-scores

Table 11: Distribution of participants' z-scores for PBDEs for milk powder (2301-MP)

Percentage of participants' results	$\lvert z\text{-score} \rvert \leq 2$	$2 < \lvert z\text{-score} \rvert < 3$	$\lvert z\text{-score} \rvert \geq 3$
BDE-28	-	-	-
BDE-47	97%	3%	-
BDE-49	-	-	-
BDE-99	97%	3%	-
BDE-100	97%	3%	-
BDE-153	93%	7%	-

Percentage of participants' results	|z-score| ≤ 2	2 < |z-score| < 3	|z-score| ≥ 3
BDE-154	100%	-	-
BDE-183	93%	7%	-
BDE-209	-	-	-
Sum of 8 PBDEs without BDE-209 (ub)	100%	-	-
Sum of 8 PBDE including BDE-209 (lb)	100%	-	-
Sum of 9 PBDE including BDE-209 (ub)	100%	-	-
Sum of 9 PBDE including BDE-209 (lb)	95%	5%	-

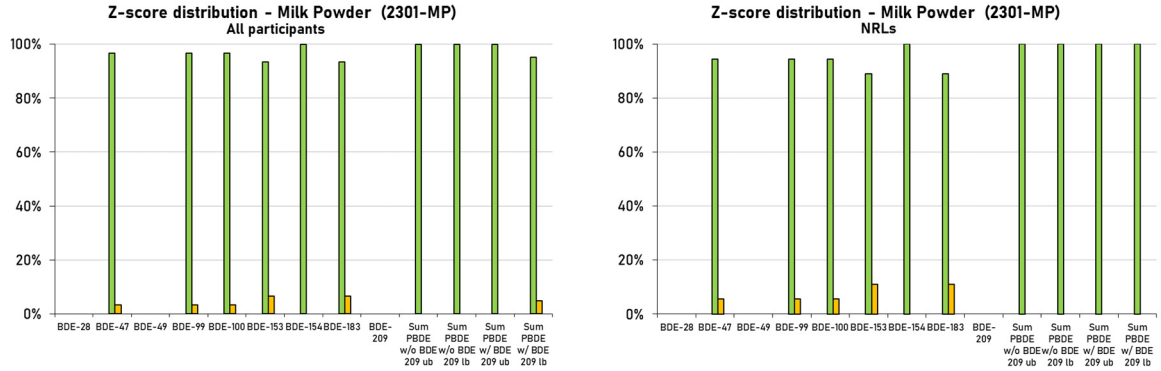


Figure 6: Distribution of participants' z-scores and NRLs only for PBDE congeners / sum parameters for milk powder (2301-MP) [Green bars: -2 ≤ z-score ≤ 2, orange bars: -3 < z-score < -2, 2 < z-score < 3, red bars: z-score ≤ -3, z-score ≥ 3]

5.3. HBCDDs - Participants' z-scores

HBCDD stereoisomers undergo thermal isomerization at temperatures above 160 °C. With GC elution temperature of these compounds of normally above 160 °C a separation of HBCDD stereoisomers using GC analysis is not possible. Only one unresolved peak is obtained. Additional thermal decomposition of HBCDDs is reported for temperatures above 240 °C. Therefore, in case of applying GC-MS methods for HBCDD analysis determination of total HBCDD (as sum of all originally present HBCDD diastereomers) is possible only.

Due to the low numbers of results for total HBCDD the sum of α-, β-, γ-HBCDD (using LC separation) was taken for comparison.

Table 12: Distribution of participants' z-scores for HBCDD for milk powder (2301-MP)

Percentage of participants' results	|z-score| ≤ 2	2 < |z-score| < 3	|z-score| ≥ 3
α - HBCDD	88%	6%	6%
β-, HBCDD	77%	8%	15%
Sum of α-, β-, γ-HBCDD (ub)	83%	6%	11%
Total HBCDD*	50%	50%	-

*Comparison of participants' results for total HBCDD with assigned value for sum of α-, β-, γ-HBCDD

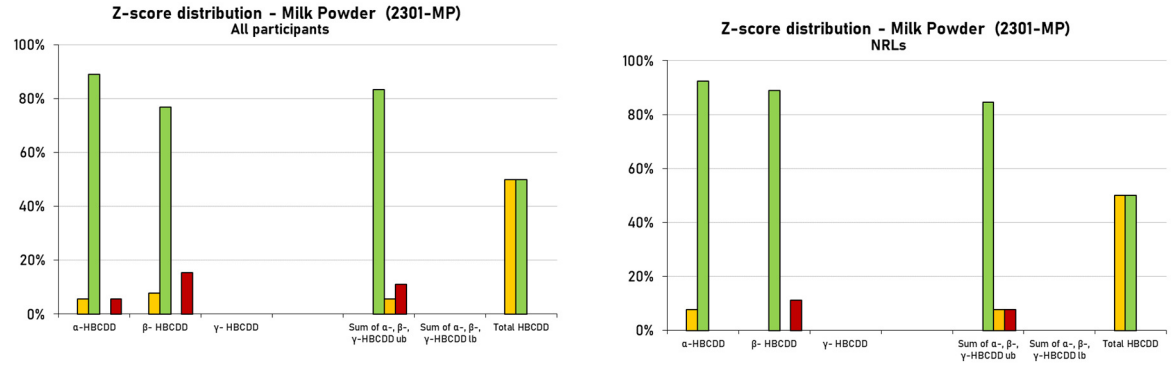


Figure 7: Distribution of participants' z-scores and NRLs only for HBCDD stereoisomers / sum parameters for milk powder (2301-MP) [Green bars: -2 ≤ z-score ≤ 2, orange bars: -3 < z-score <-2, 2 < z-score < 3, red bars: z-score ≤ -3, z-score ≥ 3]

6. Participants' feedback

A questionnaire for feedback from participants of this EURL proficiency test was available as online survey between 15 May 2023 and 23 June 2023. The survey was anonymous, but participants could also give their laboratory name. The identity of the laboratories is kept confidential. The survey included several questions related to different topics (participants' information, organization of the proficiency test, PT test samples and evaluation of results and summary of data) and a possibility to include comments and further suggestions. In total, 2 laboratories (1.5 % of all PT participants) replied to this survey.

Table 13: Participating laboratories in the feedback survey

Type of laboratory	Answers
National Reference Laboratory (NRL)	0
Official Laboratory (OFL)	0
Commercial laboratory	2
Other (e.g. research and development)	0
No Answer	0

General aspects

How satisfied are you with the organization of this proficiency test in general? Please rate the parts below according to your experience, with 0 stars meaning "no opinion" and 5 stars meaning "full satisfaction".

Announcement

Instructions

Sample shipment

Reporting of results

Preliminary report

Specific aspects of this proficiency test

We would like to know a bit more about specific aspects of this proficiency test. Please rate the aspects below according to your experience, with 0 stars meaning "no opinion" and 5 stars meaning "full satisfaction".

Was all necessary information for participation and performance of the PT provided in an understandable way?	
Was the time frame acceptable?	
Was the handling of EUSurvey as webtool for reporting and source of instructions manageable?	
Was the evaluation of participant's results and the information in the preliminary report clear and comprehensible?	

Additional comments:

- report was very comprehensive and good; convoluted structure of the document does make it difficult to read
- it is easier with the webtool than sending email with an excel file
- the delay to give the preliminary results was very short

Was the selected sample adequate for the goal to assess analytical performance of laboratories in relevant matrices?

Choice of matrix	
Level of contamination	

7. Quality control

The Deutsche Akkreditierungsstelle GmbH attests that the provider of proficiency testing Chemisches und Veterinäruntersuchungsamt Freiburg, EU Reference Laboratory (EURL) for halogenated persistent organic pollutants (POPs) in feed and food is competent under the terms of DIN EN ISO/IEC 17043:2010 to carry out proficiency testing in the testing field of determination of halogenated persistent organic pollutants (POPs) in food and feed (Accreditation number: D-EP-18625-01-00).

8. Results of participants

An overview of the PBDE and HBCDD results for the PT test sample milk powder (2301-MP) are given in the following annexes. Laboratories are coded according to the laboratory codes sent after registration.

9. References

[1] ISO 13528:2022, Statistical methods for use in proficiency testing by interlaboratory comparisons, International Organization for Standardization

[2] M. Thompson, S.L.R. Ellison, R. Wood: The International Harmonized Protocol For The Proficiency Testing Of Analytical Chemistry Laboratories, Pure Appl. Chem., Vol. 78, No. 1, pp. 145-196, 2006.

10. Annex

Milk Powder – 2301-MP	
1	Assigned and median values –PBDEs, HBCDDs and lipid content
2	Participants' results – Tables – PBDEs, HBCDDs and lipid content
3	Participants' z-scores – Tables – PBDEs, HBCDDs and lipid content
4	Participants' z-scores – Charts – PCDD/F, PCB
5	Homogeneity and stability test – PBDE
6	Overview participants' methods – Weighed sample, internal and recovery standards and comments
7	Overview participants' methods – Extractions, clean-up and detection
8	Overview participants' methods – Measurement uncertainty and Limit of Quantification

EURL for halogenated POPs in Feed and Food
c/o State Institute for Chemical and Veterinary Analysis of Food Freiburg

Coordinator: Theresa Zwickel
(Senior scientist at EURL POPs)
Phone: +49 761 8855 500 E-Mail: eurl-pops@cvuafr.bwl.de

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
11 March 2024

Annex 1: Assigned values of PBDEs and HBCDDs

Test sample - Milk Powder (2301-MP)

Assigned values of sum parameters and individual congeners

Estimation of the assigned value as the consensus of participants' results
Assigned value = Huber robust mean after exlusion of extreme outliers

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
PBDE - Assigned values

Analyte		Result µg/kg wet weight	**Assigned value** [outliers removed]	**Robust standard deviation** [outliers removed]	**Standard uncertainty** [outliers removed]	**No. of results contributing to assigned value**	**Median** [all values]
BDE-28	2,2′,4-tribromodiphenyl ether						0.00205
BDE-47	2,2′,4,4′-tetrabromodiphenyl ether		0.189	0.019	0.0042	30	0.184
BDE-49	2,2′,4,5′-tetrabromodiphenyl ether						0.00519
BDE-99	2,2′,4,4′,5-pentabromodiphenyl ether		0.256	0.031	0.0070	30	0.254
BDE-100	2,2′,4,4′,6-pentabromodiphenyl ether		0.0528	0.0051	0.0012	30	0.0527
BDE-153	2,2′,4,4′,5,5′-hexabromodiphenyl ether		0.0378	0.0035	0.00081	29	0.0379
BDE-154	2,2′,4,4′,5,6′-hexabromodiphenyl ether		0.0228	0.0028	0.00063	30	0.0228
BDE-183	2,2′,3,4,4′,5′,6-heptabromodiphenyl ether		0.0889	0.011	0.0025	30	0.0883
BDE-209	2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether						0.181
Sum of 8 PBDE	without BDE-209 (ub)		0.652	0.050	0.012	27	0.641
Sum of 8 PBDE	without BDE-209 (lb)		0.652	0.050	0.012	26	0.642
Sum of 9 PBDE	including BDE-209 (ub)		0.856	0.10	0.027	21	0.838
Sum of 9 PBDE	including BDE-209 (lb)		0.822	0.12	0.034	21	0.799

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
HBCDD - Assigned values

Analyte		Result µg/kg wet weight	**Assigned value** [outliers removed]	**Robust standard deviation** [outliers removed]	**Standard uncertainty** [outliers removed]	**No. of results contributing to assigned value**	**Median** [all values]
(+/–)-α-HBCDD	(1,2,5,6,9,10-hexabromo-(1R,2R,5S,6R,9R,10S)-rel-cyclododecane)		0.162	0.028	0.0085	17	0.164
(+/–)-β- HBCDD	(1,2,5,6,9,10-hexabromo-(1R,2S,5R,6R,9R,10S)-rel-cyclododecane)		0.0185	0.0040	0.0013	14	0.0200
(+/–)-γ- HBCDD	(1,2,5,6,9,10-hexabromo-(1R,2R,5R,6S,9S,10R)-rel-cyclododecane)						0.0100
Sum of α-, β-, γ-HBCDD	(ub)		0.199	0.048	0.015	16	0.212
Sum of α-, β-, γ-HBCDD	(lb)						0.170
Total HBCDD	(using GC-methods)						0.149

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Lipid content (BFR) - Assigned value

Analyte	Result %	**Assigned value** [outliers removed]	**Robust standard deviation** [outliers removed]	**Standard uncertainty** [outliers removed]	**No. of results contributing to assigned value**	**Median** [all values]
Lipid content		9.02	0.944	0.22	29	8.97

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
11 March 2024

Annex 2: Participants' results of PBDEs and HBCDDs

Test sample - Milk Powder (2301-MP)

* Modified/additional results reported after distribution of preliminary results to all participating laboratories

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
PBDE - Results

LC	Sample	Result µg/kg wet weight	2,2',4-tribromodiphenyl ether **BDE-28**	2,2',4,4'-tetrabromodiphenyl ether **BDE-47**	2,2',4,5'-tetrabromodiphenyl ether **BDE-49**	2,2',4,4',5-pentabromodiphenyl ether **BDE-99**	2,2',4,4',6-pentabromodiphenyl ether **BDE-100**	2,2',4,4',5,5'-hexabromodiphenyl ether **BDE-153**	2,2',4,4',5,6'-hexabromodiphenyl ether **BDE-154**	2,2',3,4,4',5',6-heptabromodiphenyl ether **BDE-183**	2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether **BDE-209**	**Sum of 8 PBDE** without BDE-209 (ub)	**Sum of 8 PBDE** without BDE-209 (lb)	**Sum of 9 PBDE** including BDE-209 (ub)	**Sum of 9 PBDE** without BDE-209 (lb)
2	2301-MP		0.0021	0.197	0.0054	0.26	0.0557	0.0372	0.0249	0.103	< 0.3	0.685	0.685	0.985	0.685
3	2301-MP														
9	2301-MP		0.00171	0.178	0.00412	0.266	0.053	0.0333	0.0221	0.0858	0.147	0.644	0.644	0.791	0.791
11	2301-MP		0.00201	0.176	0.00529	0.226	0.0523	0.0386	0.0239	0.0941	0.181	0.618	0.618	0.799	0.799
12	2301-MP		< 0.005	0.188		0.236	0.0463	0.0318	0.019	0.074	0.12				
14	2301-MP		0.0071	0.166	0.0077	0.214	0.049	0.036	0.025	0.088	0.226	0.59	0.59	0.82	0.82
18	2301-MP		0.0027	0.21	0.0017	0.3	0.055	0.045	0.025	0.096	0.18	0.74	0.74	0.92	0.92
19	2301-MP		0.00178	0.177		0.243	0.0508	0.0366	0.0212	0.0885					
27	2301-MP		0.008	0.23	0.007	0.35	0.07	0.06	0.03	0.13	0.02	0.89	0.89	0.91	0.91
31	2301-MP														
34	2301-MP		0.00208	0.188	0.00659	0.277	0.0638	0.0432	0.0247	0.089	0.31	0.694	0.694	1	1
37	2301-MP		0.00219	0.179	0.00509	0.235	0.0507	0.0384	0.0225	0.0703	0.149	0.603	0.603	0.752	0.752
46	2301-MP		0.0018	0.184	0.004	0.26	0.0554	0.0369	0.0235	0.1	0.182	0.665	0.665	0.847	0.847
49	2301-MP		0.0119	0.205	< 0.01	0.27	0.053	0.038	0.025	0.081	0.43	0.694	0.684	1.12	1.11
51	2301-MP		< 0.002	0.181	0.00371	0.251	0.0486	0.0412	0.0208	0.0929	< 0.2	0.641	0.639	0.841	0.639
55	2301-MP		0.0017	0.17	0.005	0.235	0.0493	0.0396	0.0216	0.0833	0.133	0.605	0.605	0.738	0.738
58	2301-MP		0.0028	0.204	0.0058	0.262	0.056	0.036	0.023	0.095	0.172	0.685	0.685	0.857	0.857
60	2301-MP		< 0.002	0.128	0.003	0.32	0.04	0.041	0.019	0.064		0.617	0.615		
63	2301-MP		0.0022	0.199		0.265	0.056	0.0387	0.0256	0.0942		0.68	0.68		
64	2301-MP		< 1	0.27		0.37	0.077	0.055	0.032	0.13	< 10				
76	2301-MP		< 0.001	0.182		0.242	0.0504	0.0376	0.0224	0.1	< 0.0035	0.635	0.634		
77	2301-MP		0.001	0.179	0.005	0.224	0.047	0.035	0.02	0.089		0.601			
78	2301-MP		< 0.01	0.184	< 0.01	0.23	0.0507	0.0336	0.0217	0.0862	0.131	0.626	0.606	0.757	0.737
83	2301-MP		0.0151	0.2	0.0069	0.217	0.0477	0.0361	0.0193	0.0724		0.615	0.615		
88	2301-MP		0.0067	0.202	0.0069	0.249	0.0551	0.0406	0.0248	0.0877	0.483	0.673	0.673	1.16	1.16
96	2301-MP		0.00171	0.166	0.00451	0.214	0.0477	0.0347	0.0199	0.0793	0.193	0.567	0.567	0.76	0.76
98	2301-MP		0.00172	0.178	0.00347	0.256	0.0508	0.0314	0.021	0.0855	0.167	0.628	0.628	0.795	0.795
101	2301-MP		0.00195	0.244		0.298	0.0592	0.0402	0.0252	0.111	0.157	0.78	0.78	0.937	0.937
115	2301-MP		< 0.005	0.199	0.008	0.267	0.056	0.035	0.021	0.083	0.122	0.674	0.669	0.796	0.791
121	2301-MP		0.00174	0.219		0.286	0.0591	0.0388	0.0247	0.0855		0.714	0.714		
125	2301-MP		< 0.002	0.183	0.00375	0.251	0.0484	0.0419	0.0191	0.0922	< 0.2	0.641	0.639	0.838	0.639
126	2301-MP		0.00178	0.18		0.239	0.0552	0.0378	0.025	0.0804	0.211	0.618	0.618	0.829	0.829

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
HBCDD - Results

LC	Sample	Result µg/kg wet weight	(+/–)-α-HBCDD 1,2,5,6,9,10-hexabromo-(1R,2R,5S,6R,9R,10S)-rel-cyclododecane	(+/–)-β- HBCDD 1,2,5,6,9,10-hexabromo-(1R,2S,5R,6R,9R,10S)-rel-cyclododecane	(+/–)-γ- HBCDD 1,2,5,6,9,10-hexabromo-(1R,2R,5R,6S,9S,10R)-rel-cyclododecane		Sum of α-, β-, γ-HBCDD (ub)	Sum of α-, β-, γ-HBCDD (lb)	Total HBCDD (using GC-methods)
2	2301-MP								
3	2301-MP		0.154	< 0.02	< 0.04		0.214	0.154	
9	2301-MP								
11	2301-MP		0.152	0.0155	< 0.005		0.173	0.168	
12	2301-MP								0.181
14	2301-MP		0.156	< 0.1	< 0.1		0.356	0.156	
18	2301-MP		0.171	< 0.06	< 0.06		0.291	0.171	
19	2301-MP		0.17	0.02	< 0.01		0.2	0.19	
27	2301-MP		0.197	0.019	< 0.01		0.225	0.215	
31	2301-MP		0.166	< 0.03	< 0.03		0.226	0.166	
34	2301-MP		0.179	0.02	< 0.01		0.209	0.199	
37	2301-MP								
46	2301-MP		0.142	0.0189	< 0.005		0.166	0.161	
49	2301-MP								
51	2301-MP		0.2	0.021	< 0.006		0.227	0.221	
55	2301-MP		0.0891	0.0162	< 0.032		0.137	0.105	
58	2301-MP		0.115	0.01	< 0.005		0.13	0.125	
60	2301-MP								
63	2301-MP		0.172	0.0548	< 0.05		0.276	0.226	
64	2301-MP								
76	2301-MP								
77	2301-MP								
78	2301-MP		0.161	0.0224	< 0.01		0.193	0.183	
83	2301-MP								
88	2301-MP								
96	2301-MP		0.136	0.0152	0.00374		0.155	0.115	
98	2301-MP								0.117
101	2301-MP		2.75	0.42	0.0354		3.21	3.21	
115	2301-MP		0.146	< 0.01	< 0.01		0.166	0.146	
121	2301-MP								
125	2301-MP		0.204	0.0212	< 0.006		0.232	0.226	
126	2301-MP								
101*	2301-MP		0.14	0.021	0.0018		0.163	0.163	

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Lipid content - Results

LC	Sample	Result %	Lipid content PBDE	Lipid content HBCDD	Lipid content Mean
2	2301-MP		5.2		5.2
3	2301-MP			7.2	7.2
9	2301-MP		9.3		9.3
11	2301-MP		9.1	9.1	9.1
12	2301-MP		3.3		3.3
14	2301-MP		8.5	8.5	8.5
18	2301-MP		9.0		9.0
19	2301-MP		9.7	9.7	9.7
27	2301-MP		9.8	9.8	9.8
31	2301-MP			5.7	5.7
34	2301-MP		9.7	9.7	9.7
37	2301-MP		8.7		8.7
46	2301-MP		8.4	9.5	9.0
49	2301-MP				
51	2301-MP		8.6	8.6	8.6
55	2301-MP		8.7	8.7	8.7
58	2301-MP		8.6	8.6	8.6
60	2301-MP		9.9		9.9
63	2301-MP		9.6	9.6	9.6
64	2301-MP		10.6		10.6
76	2301-MP		8.9		8.9
77	2301-MP		9.9		9.9
78	2301-MP		9.8	9.8	9.8
83	2301-MP		9.1		9.1
88	2301-MP		13.4		13.4
96	2301-MP		5.3	5.3	5.3
98	2301-MP		8.5	8.5	8.54
101	2301-MP		9.8	9.8	9.8
115	2301-MP		7.8	7.8	7.8
121	2301-MP		2.8		2.79
125	2301-MP		8.6	8.6	8.6
126	2301-MP		9.7		9.7
2*	2301-MP		10.4		

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
11 March 2024

Annex 3: Participants' z-scores of PBDEs and HBCDDs - Tables

Test sample - Milk Powder (2301-MP)

Z-scores of sum parameters and individual results

Calculation of z-score on basis of assigned value

$$z = (x - x_a) / \sigma_p$$

x_a: assigned value
x: participant's result
σ_p: fitness-for-purpose-based standard deviation for proficiency assessment
20%: Evaluated individual PBDE congeners and HBCDD diastereomers and sum

* Modified/additional results reported after distribution of preliminary results to all participating laboratories

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

PBDE - Z-scores

LC	Sample	Z-score [σ_p = 20 %]	2,2',4-tribromodiphenyl ether **BDE-28**	2,2',4,4'-tetrabromodiphenyl ether **BDE-47**	2,2',4,5'-tetrabromodiphenyl ether **BDE-49**	2,2',4,4',5-pentabromodiphenyl ether **BDE-99**	2,2',4,4',6-pentabromodiphenyl ether **BDE-100**	2,2',4,4',5,5'-hexabromodiphenyl ether **BDE-153**	2,2',4,4',5,6'-hexabromodiphenyl ether **BDE-154**	2,2',3,4,4',5',6-heptabromodiphenyl ether **BDE-183**	2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether **BDE-209**	**Sum of 8 PBDE** without BDE-209 (ub)	**Sum of 8 PBDE** without BDE-209 (lb)	**Sum of 9 PBDE** including BDE-209 (ub)	**Sum of 9 PBDE** without BDE-209 (lb)
2	2301-MP			0.2		0.1	0.3	-0.1	0.5	0.8		0.3	0.3	0.8	-0.8
3	2301-MP														
9	2301-MP			-0.3		0.2	0.0	-0.6	-0.2	-0.2		-0.1	-0.1	-0.4	-0.2
11	2301-MP			-0.3		-0.6	0.0	0.1	0.2	0.3		-0.3	-0.3	-0.3	-0.1
12	2301-MP			0.0		-0.4	-0.6	-0.8	-0.8	-0.8					
14	2301-MP			-0.6		-0.8	-0.4	-0.2	0.5	-0.1		-0.5	-0.5	-0.2	0.0
18	2301-MP			0.6		0.9	0.2	1.0	0.5	0.4		0.7	0.7	0.4	0.6
19	2301-MP			-0.3		-0.3	-0.2	-0.2	-0.4	0.0					
27	2301-MP			1.1		1.8	1.6	2.9	1.6	2.3		1.8	1.8	0.3	0.5
31	2301-MP														
34	2301-MP			0.0		0.4	1.0	0.7	0.4	0.0		0.3	0.3	0.8	1.1
37	2301-MP			-0.3		-0.4	-0.2	0.1	-0.1	-1.0		-0.4	-0.4	-0.6	-0.4
46	2301-MP			-0.1		0.1	0.2	-0.1	0.2	0.6		0.1	0.1	-0.1	0.2
49	2301-MP			0.4		0.3	0.0	0.0	0.5	-0.4		0.3	0.2	1.5	1.8
51	2301-MP			-0.2		-0.1	-0.4	0.4	-0.4	0.2		-0.1	-0.1	-0.1	-1.1
55	2301-MP			-0.5		-0.4	-0.3	0.2	-0.3	-0.3		-0.4	-0.4	-0.7	-0.5
58	2301-MP			0.4		0.1	0.3	-0.2	0.0	0.3		0.3	0.3	0.0	0.2
60	2301-MP			-1.6		1.3	-1.2	0.4	-0.8	-1.4		-0.3	-0.3		
63	2301-MP			0.3		0.2	0.3	0.1	0.6	0.3		0.2	0.2		
64	2301-MP			2.1		2.2	2.3	2.3	2.0	2.3					
76	2301-MP			-0.2		-0.3	-0.2	0.0	-0.1	0.6		-0.1	-0.1		
77	2301-MP			-0.3		-0.6	-0.5	-0.4	-0.6	0.0		-0.4			
78	2301-MP			-0.1		-0.5	-0.2	-0.6	-0.2	-0.2		-0.2	-0.4	-0.6	-0.5
83	2301-MP			0.3		-0.8	-0.5	-0.2	-0.8	-0.9		-0.3	-0.3		
88	2301-MP			0.3		-0.1	0.2	0.4	0.4	-0.1		0.2	0.2	1.8	2.1
96	2301-MP			-0.6		-0.8	-0.5	-0.4	-0.6	-0.5		-0.7	-0.7	-0.6	-0.4
98	2301-MP			-0.3		0.0	-0.2	-0.8	-0.4	-0.2		-0.2	-0.2	-0.4	-0.2
101	2301-MP			1.5		0.8	0.6	0.3	0.5	1.2		1.0	1.0	0.5	0.7
115	2301-MP			0.3		0.2	0.3	-0.4	-0.4	-0.3		0.2	0.1	-0.4	-0.2
121	2301-MP			0.8		0.6	0.6	0.1	0.4	-0.2		0.5	0.5		
125	2301-MP			-0.2		-0.1	-0.4	0.5	-0.8	0.2		-0.1	-0.1	-0.1	-1.1
126	2301-MP			-0.2		-0.3	0.2	0.0	0.5	-0.5		-0.3	-0.3	-0.2	0.0

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
HBCDD - Z-scores

LC	Sample	Z-score [σ_p = 20 %]	**(+/–)-α-HBCDD** 1,2,5,6,9,10-hexabromo-(1R,2R,5S,6R,9R,10S)-rel-cyclododecane	**(+/–)-β- HBCDD** 1,2,5,6,9,10-hexabromo-(1R,2S,5R,6R,9R,10S)-rel-cyclododecane	**(+/–)-γ- HBCDD** 1,2,5,6,9,10-hexabromo-(1R,2R,5R,6S,9S,10R)-rel-cyclododecane	**Sum of α-, β-, γ-HBCDD** (ub)	**Sum of α-, β-, γ-HBCDD** (lb)	**Total HBCDD*** (using GC-methods)
2	2301-MP							
3	2301-MP		-0.2			0.4		
9	2301-MP							
11	2301-MP		-0.3	-0.8		-0.7		
12	2301-MP							-0.5
14	2301-MP		-0.2			3.9		
18	2301-MP		0.3			2.3		
19	2301-MP		0.2	0.4		0.0		
27	2301-MP		1.1	0.1		0.7		
31	2301-MP		0.1			0.7		
34	2301-MP		0.5	0.4		0.3		
37	2301-MP							
46	2301-MP		-0.6	0.1		-0.8		
49	2301-MP							
51	2301-MP		1.2	0.7		0.7		
55	2301-MP		-2.3	-0.6		-1.6		
58	2301-MP		-1.5	-2.3		-1.7		
60	2301-MP							
63	2301-MP		0.3	9.8		1.9		
64	2301-MP							
76	2301-MP							
77	2301-MP							
78	2301-MP		0.0	1.1		-0.2		
83	2301-MP							
88	2301-MP							
96	2301-MP		-0.8	-0.9		-1.1		
98	2301-MP							-2.1
101	2301-MP		79.9	108.5		75.7		
115	2301-MP		-0.5			-0.8		
121	2301-MP							
125	2301-MP		1.3	0.7		0.8		
126	2301-MP							
101*	2301-MP		-0.7	0.7		-0.9		

* Z-scores for information only; calculation based on assigned value for sum of α-, β-, γ-HBCDD (ub)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Lipid content - Results

LC	Sample	Z-score [σ_p = 10 %]	Lipid content PBDE	Lipid content HBCDD	Lipid content Mean
2	2301-MP		-4.2		-4.2
3	2301-MP			-2.0	-2.0
9	2301-MP		0.3		0.3
11	2301-MP		0.1	0.1	0.1
12	2301-MP		-6.3		-6.3
14	2301-MP		-0.6	-0.6	-0.6
18	2301-MP		0.0		0.0
19	2301-MP		0.8	0.8	0.8
27	2301-MP		0.9	0.9	0.9
31	2301-MP			-3.7	-3.7
34	2301-MP		0.7	0.7	0.7
37	2301-MP		-0.4		-0.4
46	2301-MP		-0.6	0.5	-0.1
49	2301-MP				
51	2301-MP		-0.4	-0.4	-0.4
55	2301-MP		-0.4	-0.4	-0.4
58	2301-MP		-0.5	-0.5	-0.5
60	2301-MP		1.0		1.0
63	2301-MP		0.6	0.6	0.6
64	2301-MP		1.8		1.8
76	2301-MP		-0.1		-0.1
77	2301-MP		1.0		1.0
78	2301-MP		0.8	0.8	0.8
83	2301-MP		0.1		0.1
88	2301-MP		4.9		4.9
96	2301-MP		-4.1	-4.1	-4.1
98	2301-MP		-0.5	-0.5	-0.5
101	2301-MP		0.9	0.9	0.9
115	2301-MP		-1.4	-1.4	-1.4
121	2301-MP		-6.9		-6.9
125	2301-MP		-0.4	-0.4	-0.4
126	2301-MP		0.7		0.7
2*	2301-MP		1.5		

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
11 March 2024

Annex 4: Participants' z-scores of PBDEs and HBCDDs - Charts

Test sample - Milk Powder (2301-MP)

Z-scores of sum parameters and individual results

Calculation of z-score on basis of assigned value

$$z = (x - x_a) / \sigma_p$$

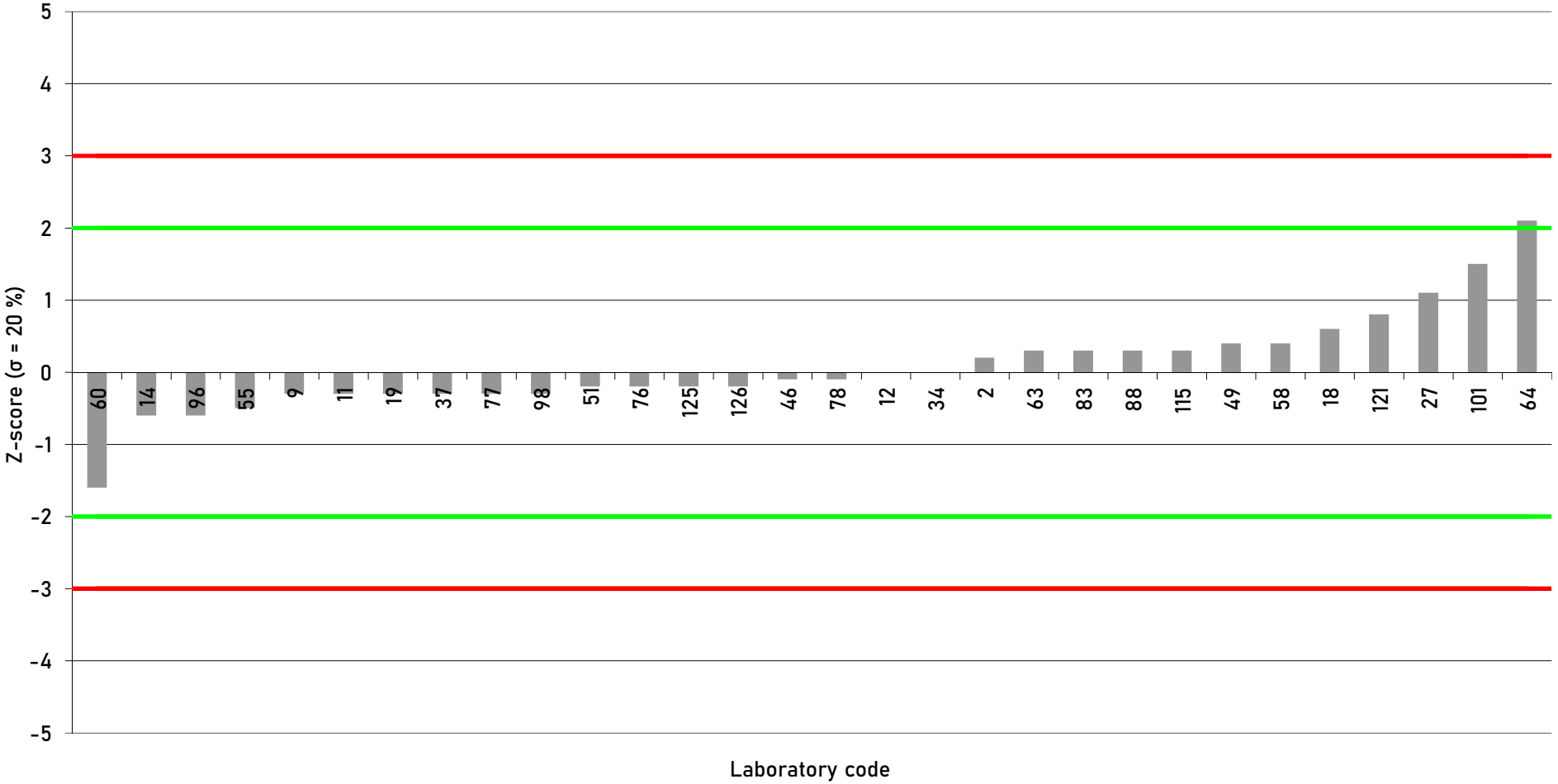
x_a: assigned value
x: participant's result
σ_p: fitness-for-purpose-based standard deviation for proficiency assessment
20%: Evaluated individual PBDE congeners and HBCDD diastereomers and sum

± 2 z-scores:
± 3 z-scores:

Milk Powder (2301-MP)

BDE-47

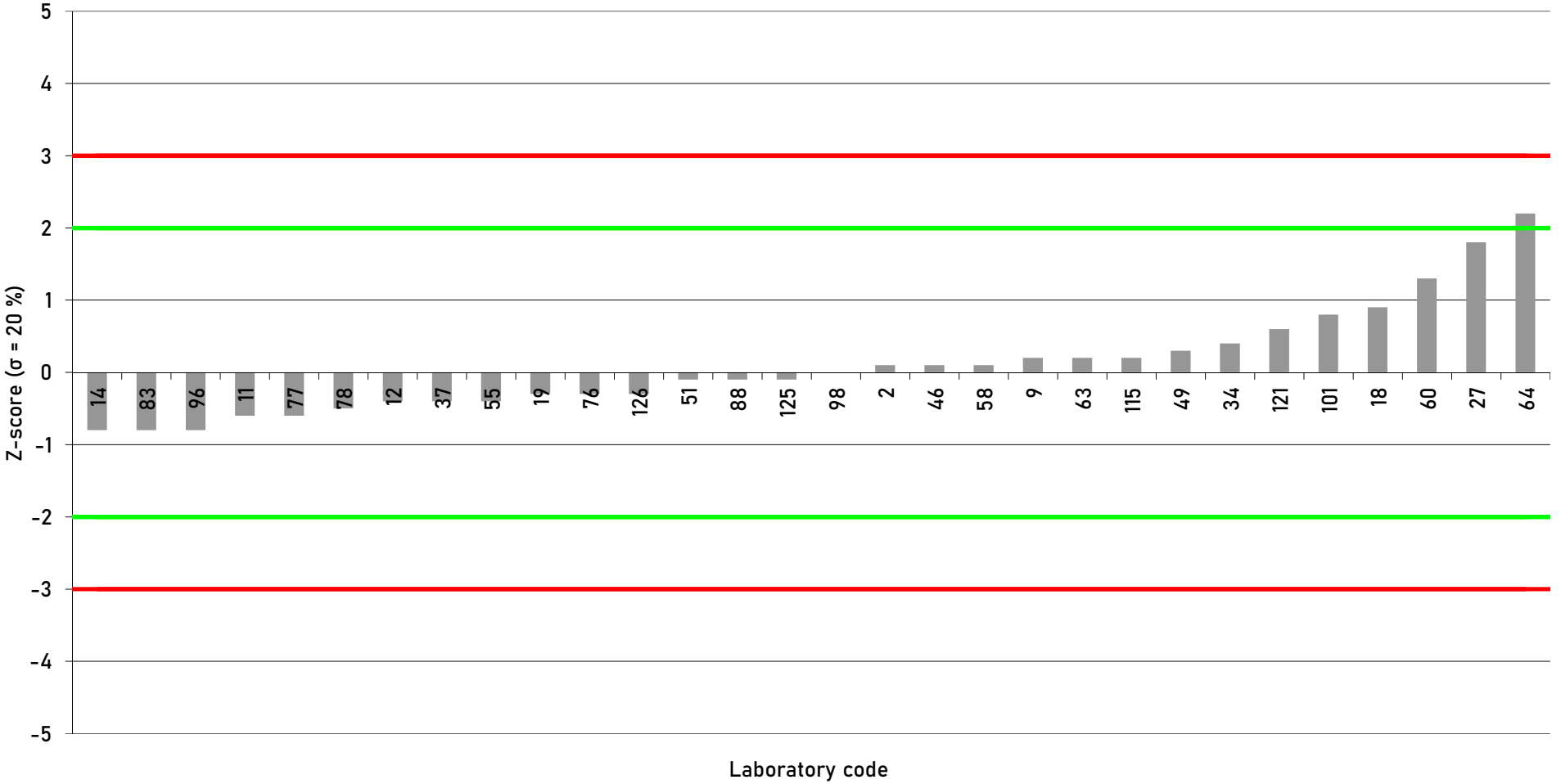
Assigned value: 0.189 µg/kg wet weight



Milk Powder (2301-MP)

BDE-99

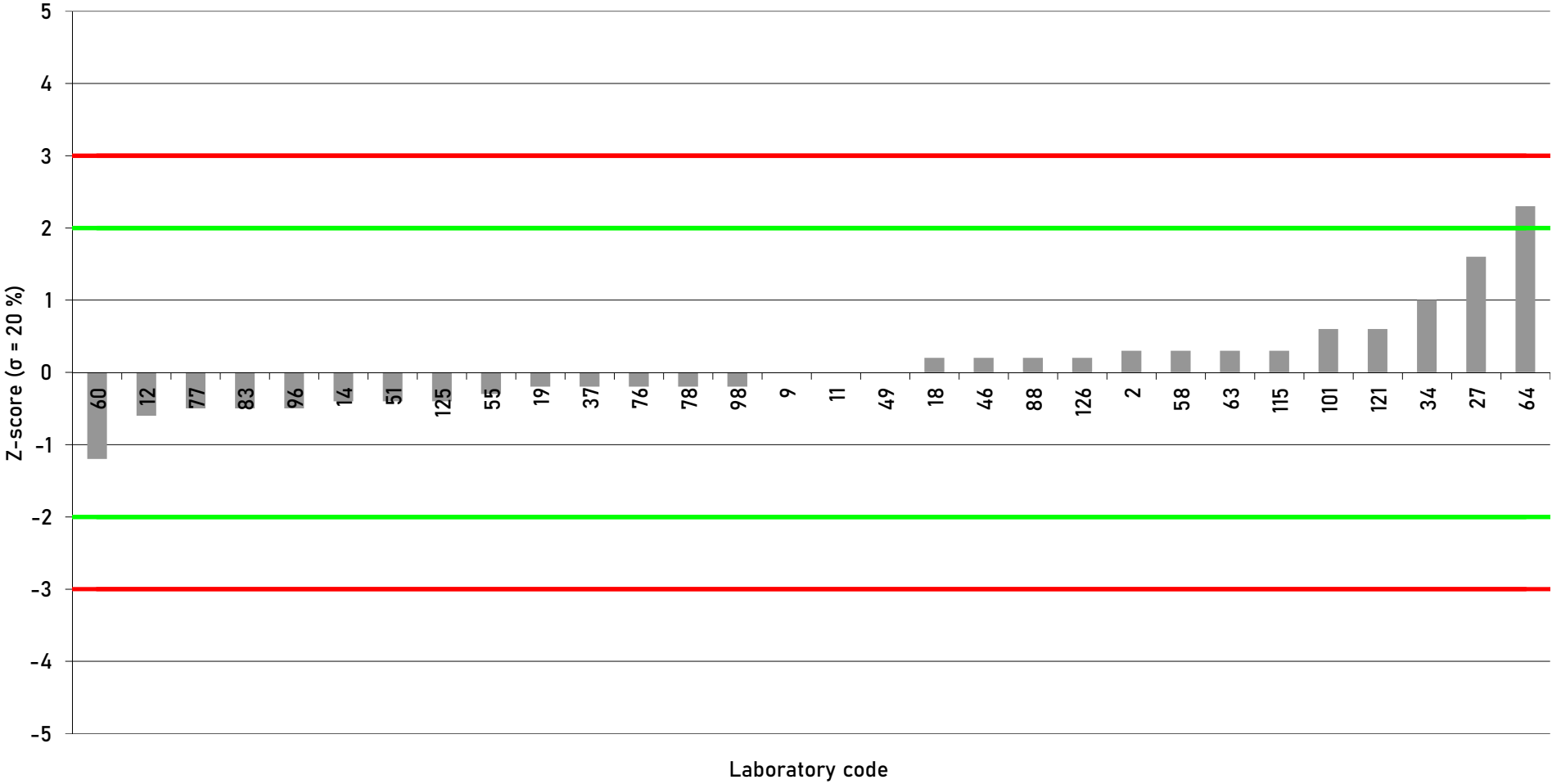
Assigned value: 0.256 µg/kg wet weight



Milk Powder (2301-MP)

BDE-100

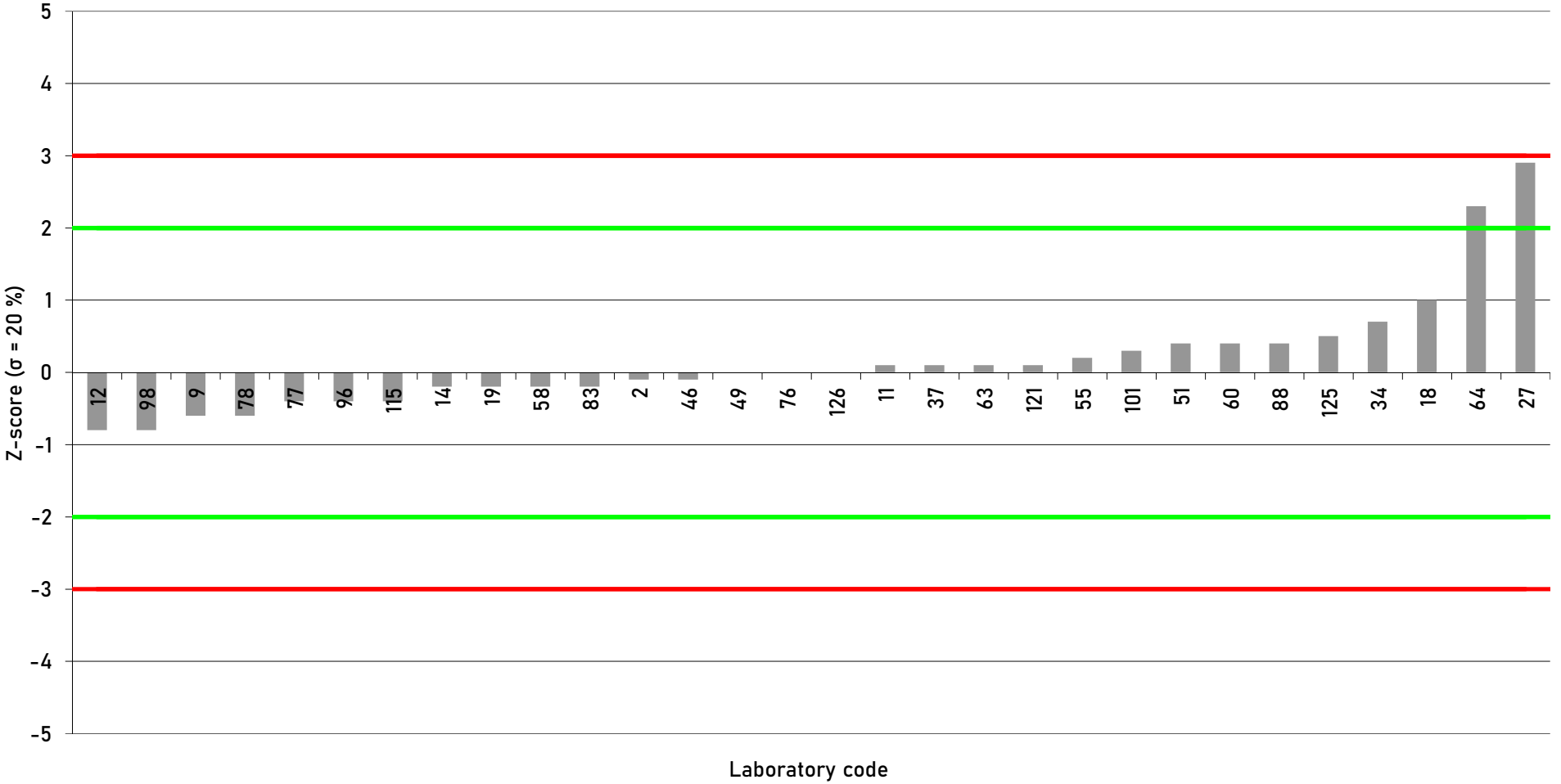
Assigned value: 0.0528 µg/kg wet weight



Milk Powder (2301-MP)

BDE-153

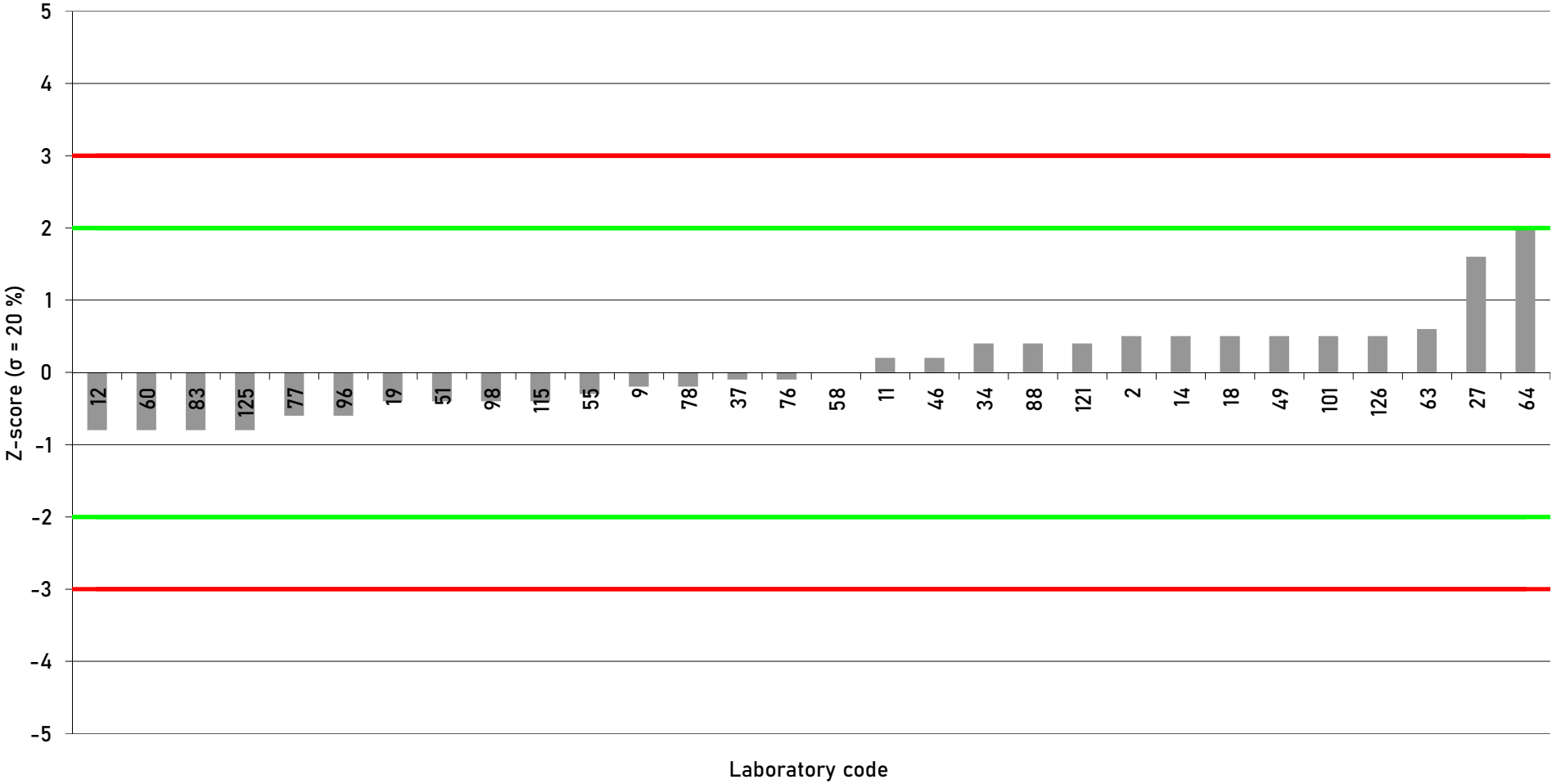
Assigned value: 0.0378 µg/kg wet weight



Milk Powder (2301-MP)

BDE-154

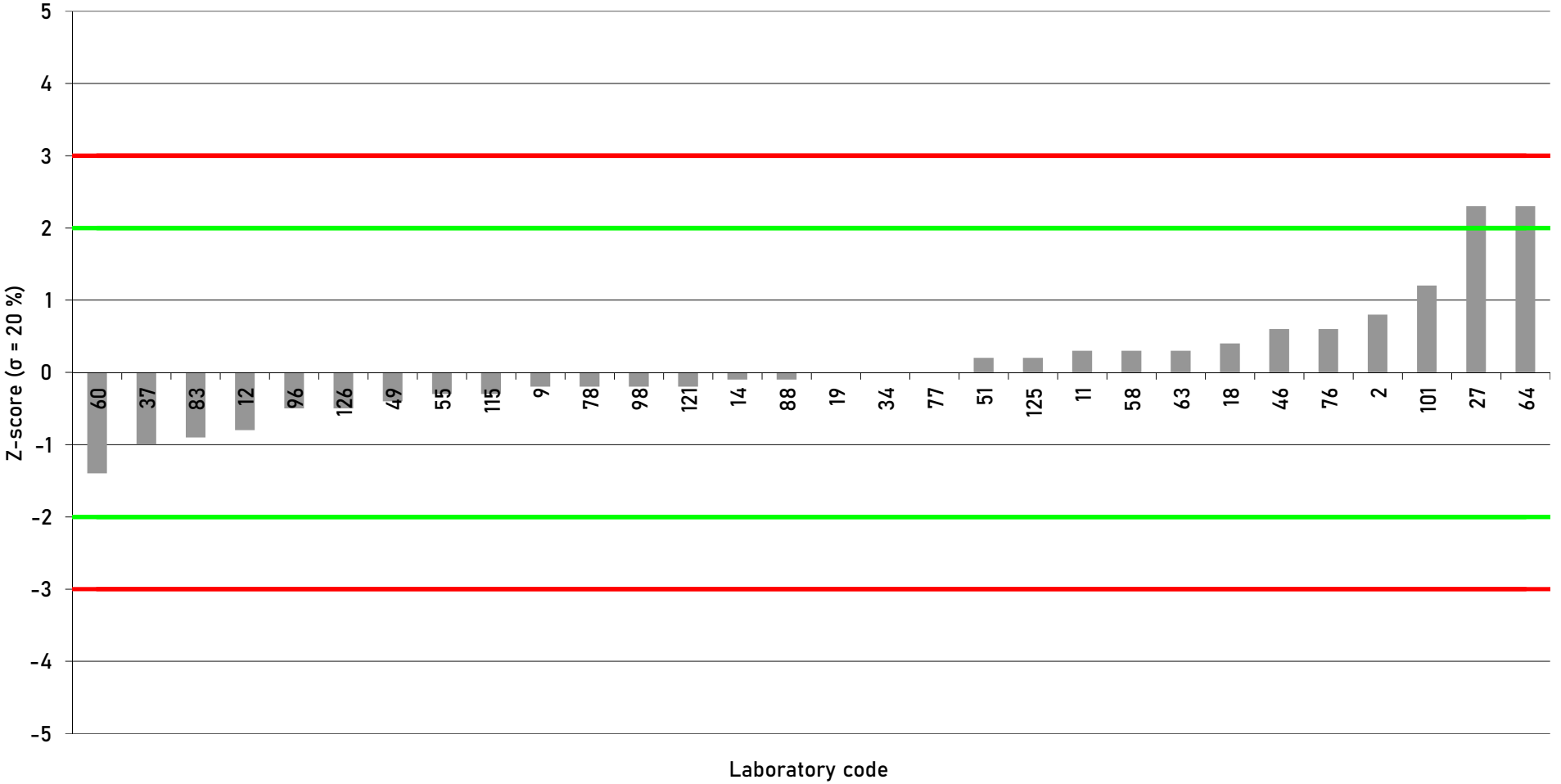
Assigned value: 0.0228 µg/kg wet weight



Milk Powder (2301-MP)

BDE-183

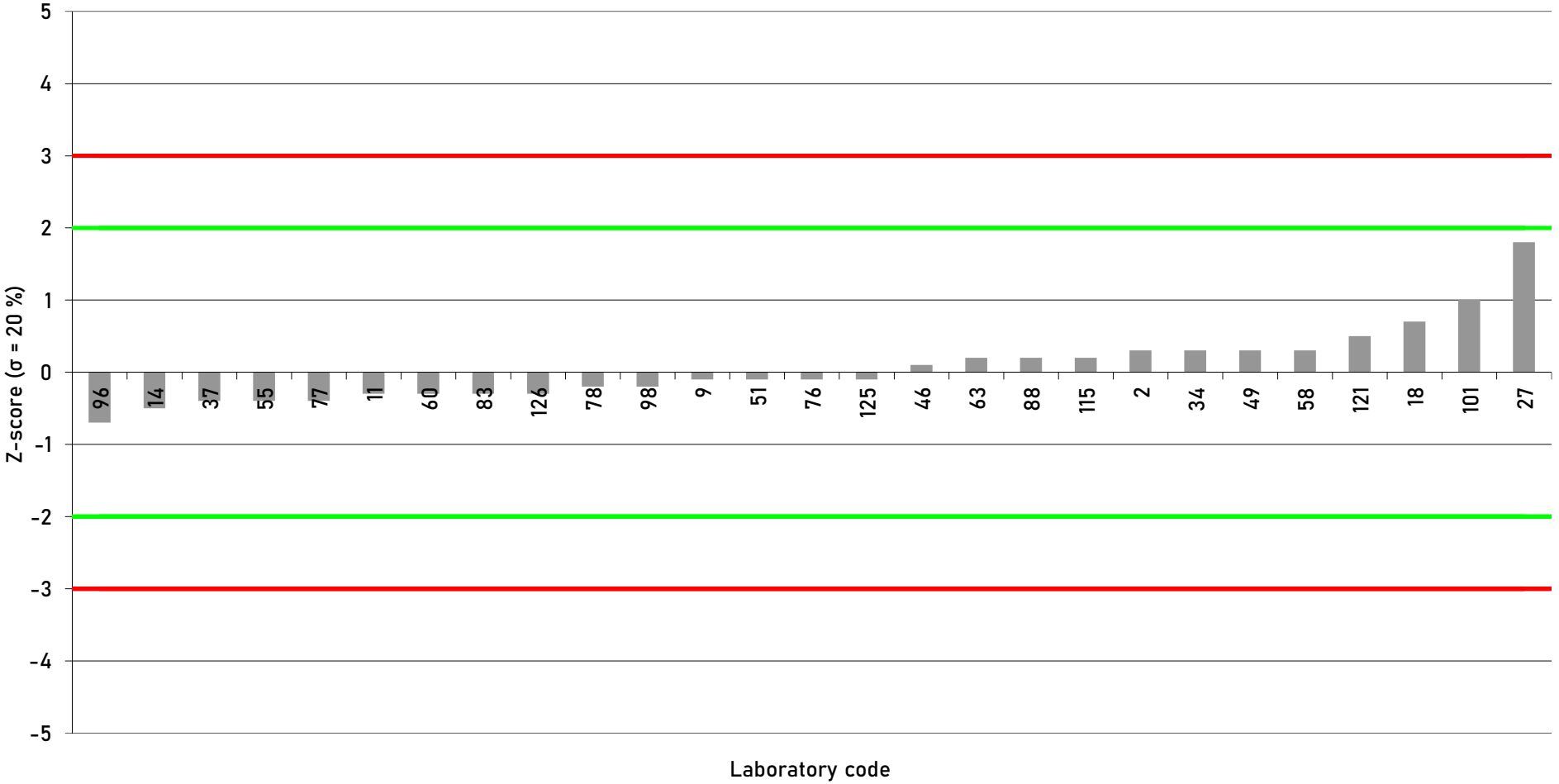
Assigned value: 0.0889 µg/kg wet weight



Milk Powder (2301-MP)

Sum of PBDE without BDE-209 ub

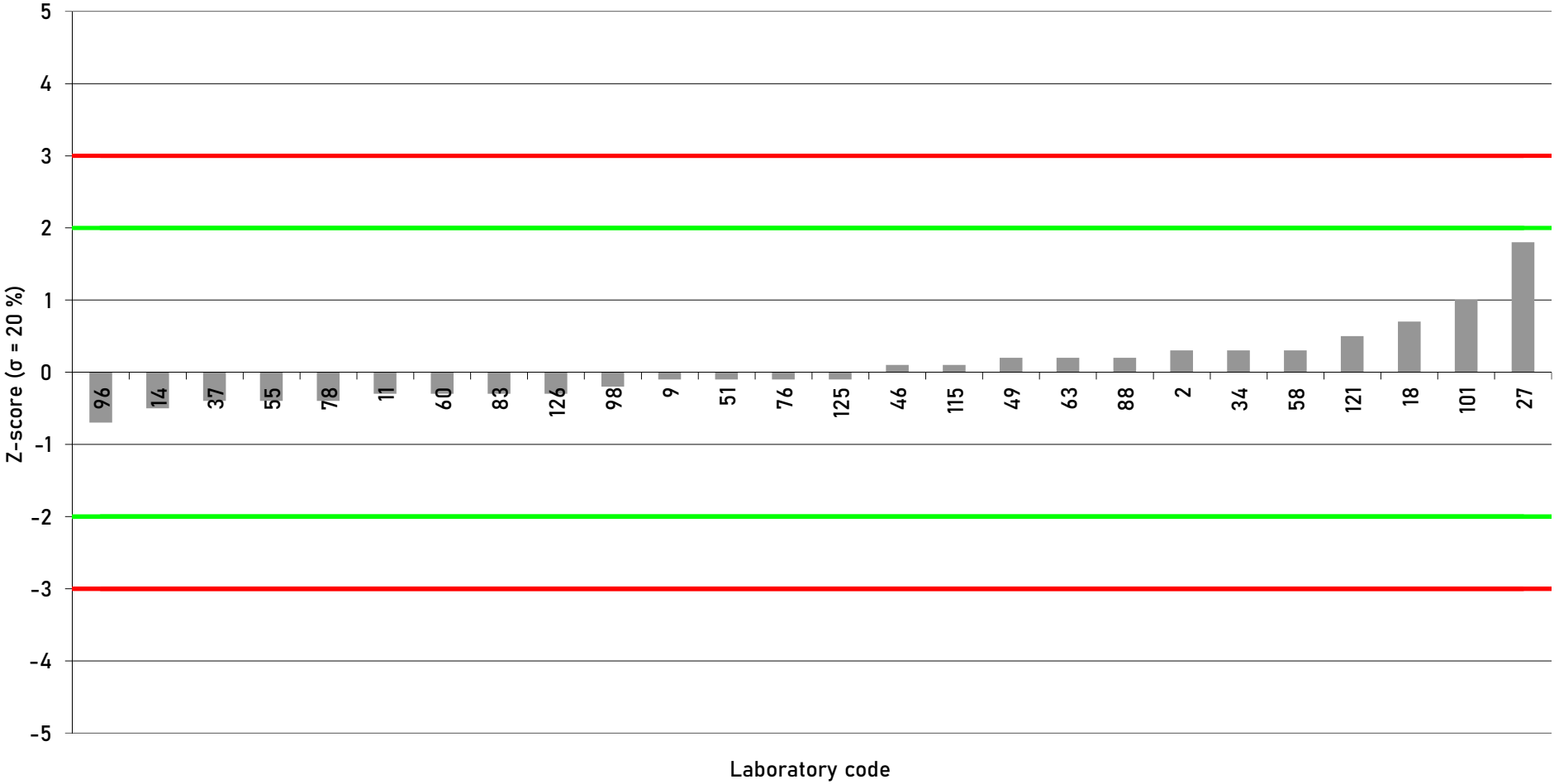
Assigned value: 0.652 µg/kg wet weight



Milk Powder (2301-MP)

Sum of PBDE without BDE-209 lb

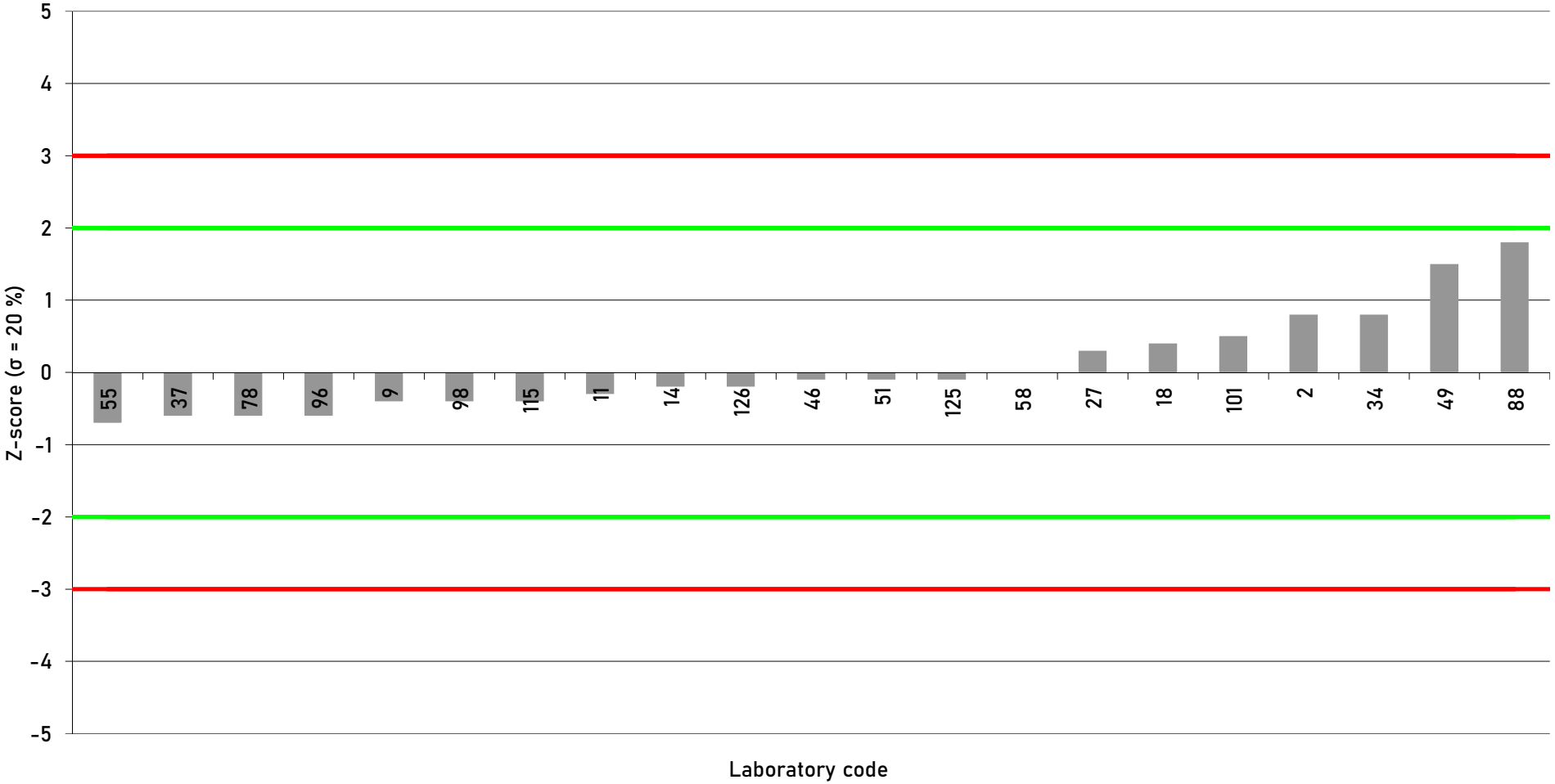
Assigned value: 0.652 µg/kg wet weight



Milk Powder (2301-MP)

Sum of PBDE including BDE-209 ub

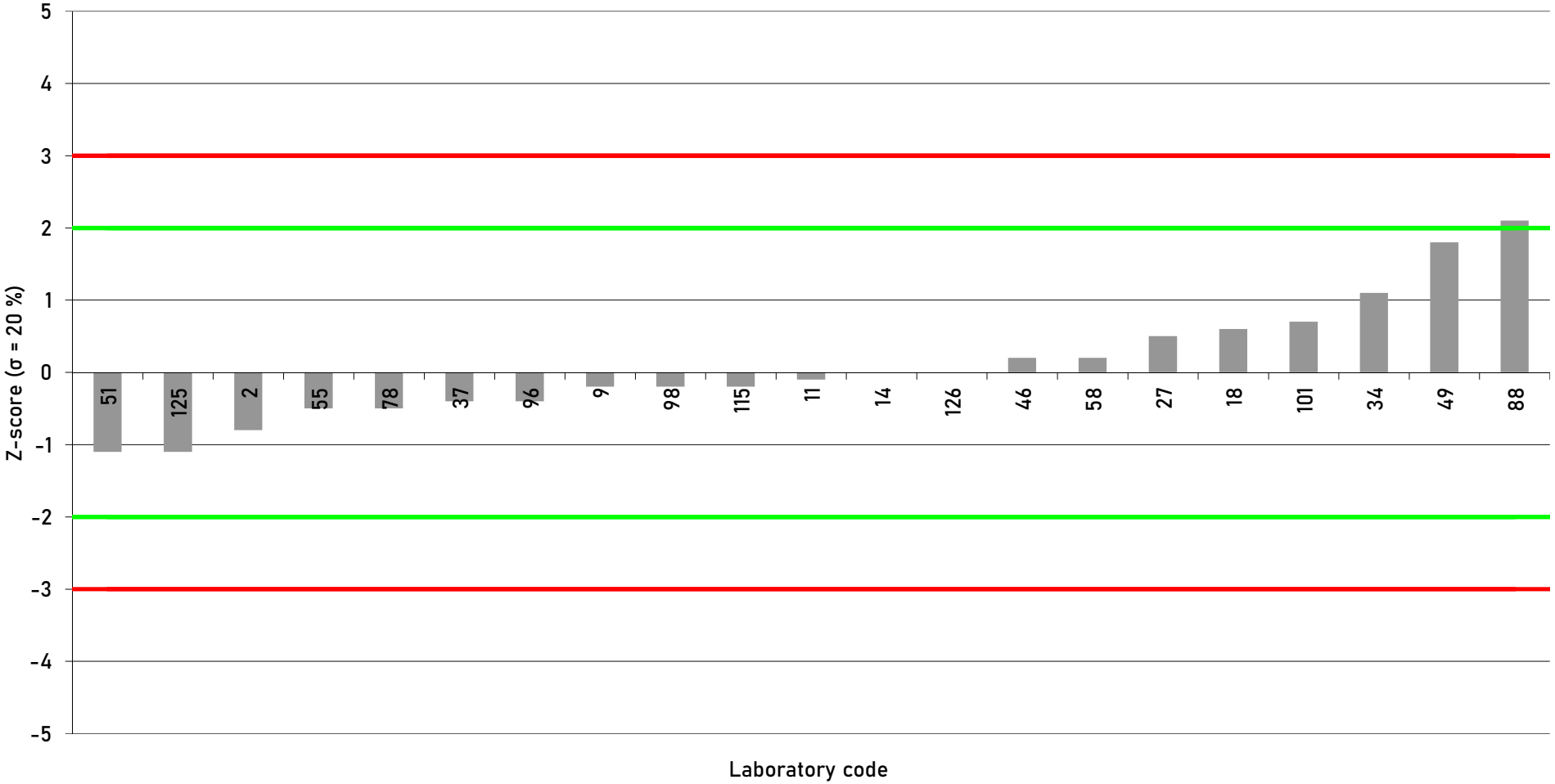
Assigned value: 0.856 µg/kg wet weight



Milk Powder (2301-MP)

Sum of PBDE including BDE-209 lb

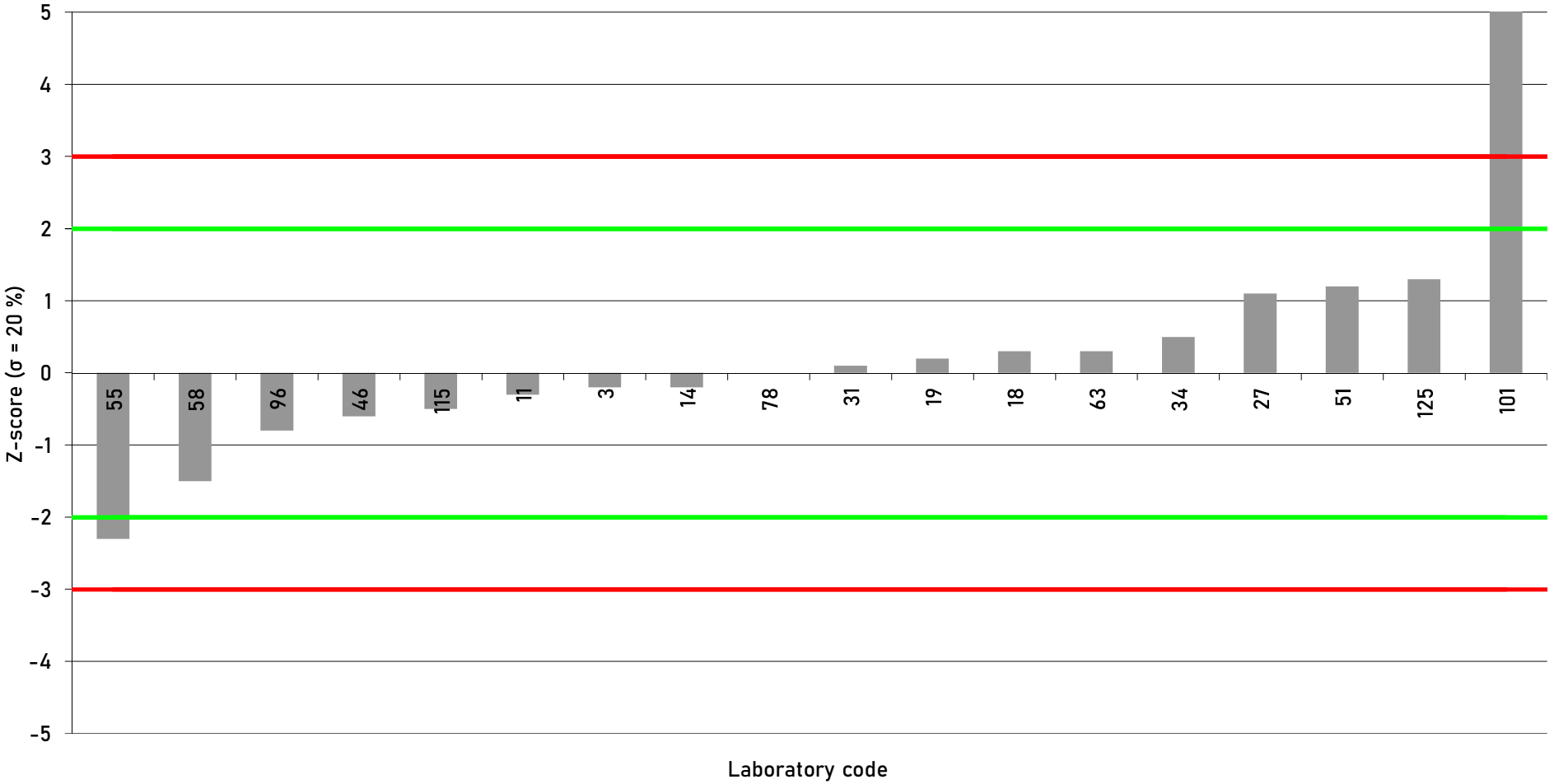
Assigned value: 0.822 µg/kg wet weight



Milk Powder (2301-MP)

(+/-)-α-HBCDD

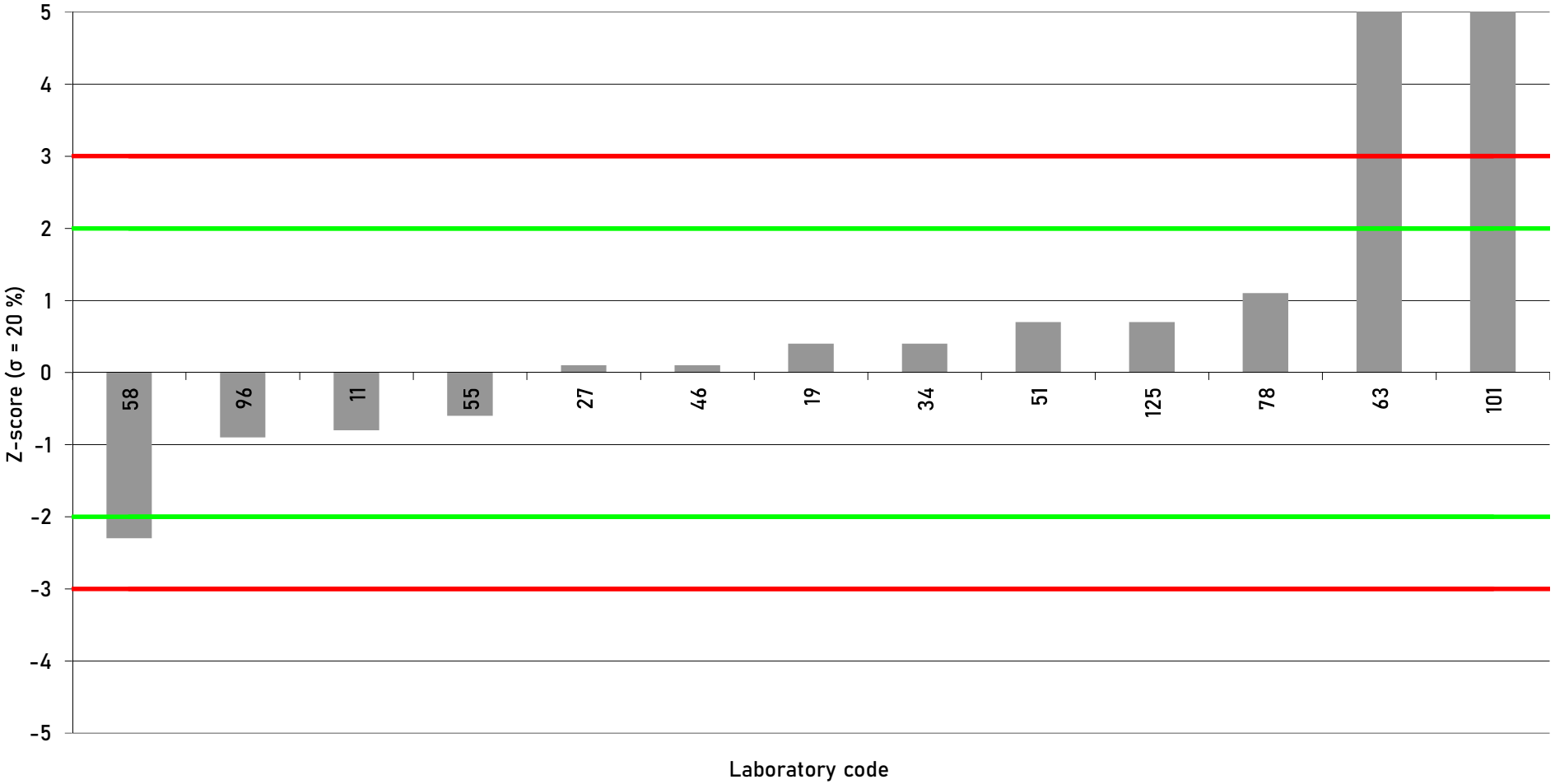
Assigned value: 0.162 µg/kg wet weight



Milk Powder (2301-MP)

(+/–)-β- HBCDD

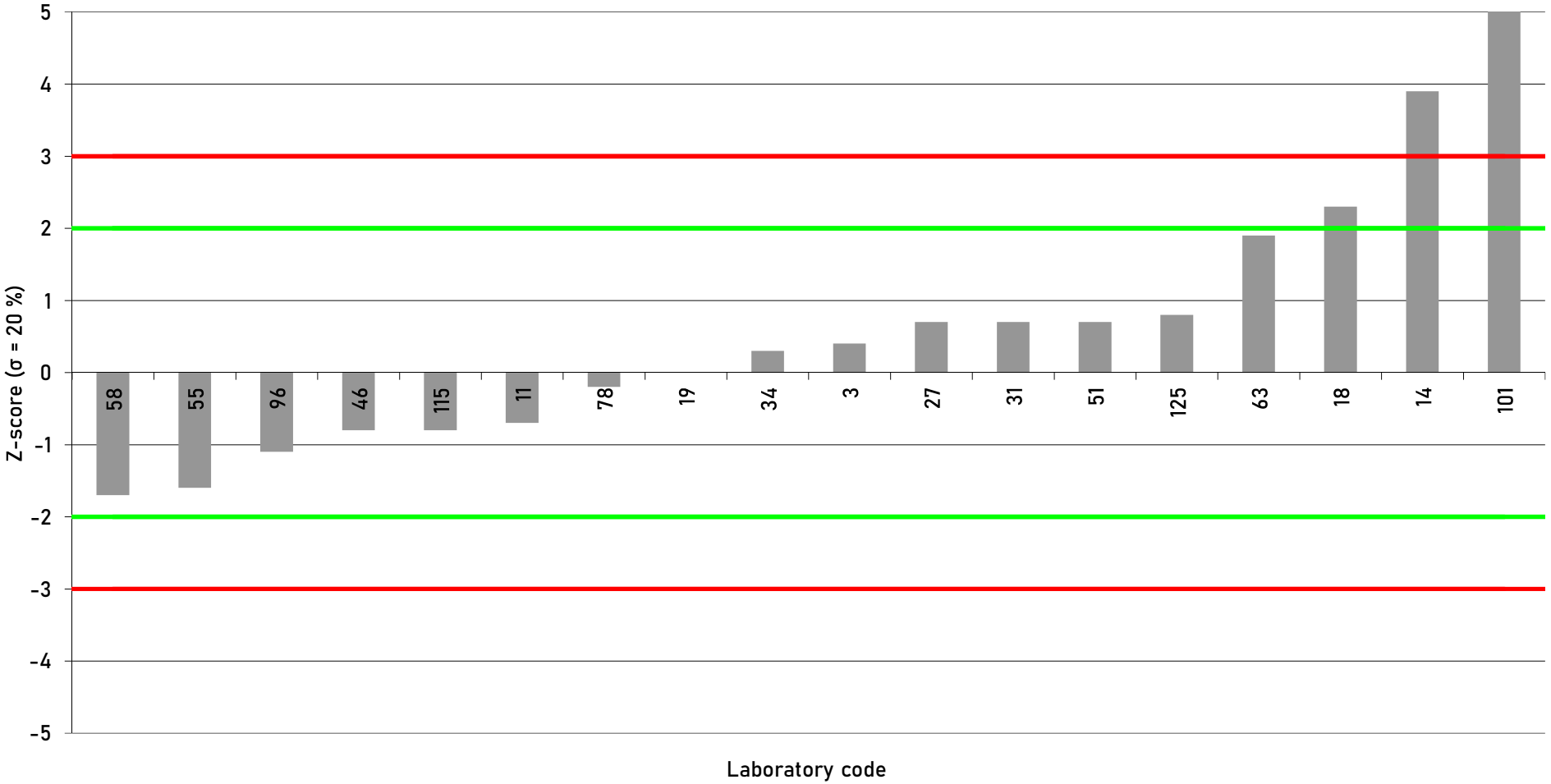
Assigned value: 0.0185 µg/kg wet weight



Milk Powder (2301-MP)

Sum of α-, β-, γ-HBCDD ub

Assigned value: 0.199 µg/kg wet weight



EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
11 March 2024

Annex 5: Test for sufficient homogeneity and stability for PBDEs

Test sample - Milk Powder (2301-MP)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for Halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
PBDE - Homogeneity test - Data

Analyte	Result µg/kg wet weight	**Mean** (n = 10, duplicate analysis)	**Median** (n = 10, duplicate analysis)	**Relative standard deviation** [%]
Sum of PBDE without BDE-209 ub		0.631	0.640	5%
Sum of PBDE including BDE-209 ub		0.788	0.794	5%
BDE-28		0.00171	0.00173	6%
BDE-47		0.181	0.183	4%
BDE-49		0.00262	0.00265	14%
BDE-99		0.248	0.251	6%
BDE-100		0.0564	0.0567	7%
BDE-153		0.0360	0.0364	6%
BDE-154		0.0233	0.0234	6%
BDE-183		0.0813	0.0825	5%
BDE-209		0.157	0.161	13%

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for Halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Selected PBDE congeners - Homogeneity test - Data

Sample	Replicate	Result µg/kg wet weight	**BDE-183**
5	1		0.082
	2		0.080
8	1		0.086
	2		0.078
66	1		0.080
	2		0.084
79	1		0.086
	2		0.070
103	1		0.078
	2		0.086
116	1		0.083
	2		0.084
120	1		0.078
	2		0.079
146	1		0.081
	2		0.084
202	1		0.083
	2		0.087
210	1		0.074
	2		0.083
Cochran's C-test			
C			0.506
$C_{critical}$ (α = 0.05, m = 2, n = 10)			0.602
$C_{critical}$ (α = 0.01, m = 2, n = 10)			0.718
$C < C_{critical}$			yes
Outliers			no evidence for analytical outliers
Homogeneity test			
General average $\bar{x}$			0.081
Standard deviation of sample averages s_x			0.0023
Wthin-sample standard deviation s_w			0.0048
Between-sample standard deviation s_s			0.0000
Standard deviation for proficiency assessment σ_{PT}			0.0163
s_s / σ_{PT}			0.0
Test for homogeneity ($s_s \leq 0.3\ \sigma_{PT}$)			passed

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for Halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Selected congeners - Stability test - Data

Sample	Replicate	Result µg/kg wet weight	**BDE-183**
6	1		0.086
	2		0.079
110	1		0.082
	2		0.085
202	1		0.083
	2		0.087
Stability test			
General average (stability test) $\bar{y}$			0.084
General average (homogeneity test) $\bar{x}$			0.081
Standard deviation for proficiency assessment σPT			0.0163
$\lvert \bar{y} - \bar{x} \rvert$			0.00235
Test for stability ($\lvert \bar{y} - \bar{x} \rvert \leq 0.3$ σPT)			passed

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food
11 March 2024

Annex 6: Overview participants' methods – Weighed sample, internal and recovery standards and comments

Test sample - Milk Powder (2301-MP)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Physico-chemical Methods PBDEs - Internal standards

LC	Sample	Weighed sample [g]	Use of isotope-labelled internal standards for … PBDE congeners (yes/no)
2	2301-MP	50.01	YES (15)
3	2301-MP		
9	2301-MP	20.0	yes
11	2301-MP	20.0	yes
12	2301-MP	1	no
14	2301-MP	10.6	yes
18	2301-MP	23.3	yes
19	2301-MP	6/10 g	yes
27	2301-MP	30	yes
31	2301-MP		
34	2301-MP	50.0	yes
37	2301-MP	45.0	yes
46	2301-MP	10	yes
49	2301-MP	2.5	no
51	2301-MP	5.0	yes
55	2301-MP	11.6	yes
58	2301-MP	10	yes
60	2301-MP	30 g	yes
63	2301-MP	10.0	yes
64	2301-MP	10.0	yes
76	2301-MP	5	yes
77	2301-MP	5.95	yes
78	2301-MP	10.2	yes
83	2301-MP	34.9	yes (except for BDE-49)
88	2301-MP	18.17	yes
96	2301-MP	3	YES
98	2301-MP	30.0	yes
101	2301-MP	20.0	yes
115	2301-MP	2	yes
121	2301-MP	10	YES
125	2301-MP	5.0	yes
126	2301-MP	15.0	yes

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Methods PBDEs - Internal Standards

LC	Sample	BDE 28	BDE 47	BDE 49	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209
2	2301-MP	28	47	47	99	100	153	154	183	208
3	2301-MP									
9	2301-MP	13C BDE-28	13C BDE-47	13C BDE-47	13C BDE-99	13C BDE-100	13C BDE-153	13C BDE-154	13C BDE-183	13C BDE-209
11	2301-MP	BDE-28	BDE-47	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
12	2301-MP	13C-BDE-155	13C-BDE-155		13C-BDE-155	13C-BDE-155	13C-BDE-155	13C-BDE-155	13C-BDE-155	13C-BDE-209
14	2301-MP	13C-BDE-28	13C-BDE-47	13C-BDE-47	13C-BDE-99	13C-BDE-100	13C-BDE-153	13C-BDE-154	13C-BDE-183	13C-BDE-209
18	2301-MP	13C-BDE 28	13C-BDE 47	13C-BDE 47	13C-BDE 99	13C-BDE 100	13C-BDE 153	13C-BDE 154	13C-BDE 183	13C-BDE 209
19	2301-MP	L-BDE-28 (13C)	L-BDE-47 (13C)	L-BDE-47 (13C)	L-BDE-99 (13C)	L-BDE-100 (13C)	L-BDE-153 (13C)	L-BDE-154 (13C)	L-BDE-183 (13C)	L-BDE-209 (13C)
27	2301-MP	13C-BDE-28	13C-BDE-47	13C-BDE-47	13C-BDE-99	13C-BDE-100	13C-BDE-153	13C-BDE-154	13C-BDE-183	13C-BDE-209
31	2301-MP									
34	2301-MP	13C-BDE-28	13C-BDE-47	13C-BDE-47	13C-BDE-99	13C-BDE-100	13C-BDE-153	13C-BDE-154	13C-BDE-183	13C-BDE-209
37	2301-MP	13C-BDE-28	13C-BDE-47	13C-BDE-47	13C-BDE-99	13C-BDE-100	13C-BDE-153	13C-BDE-154	13C-BDE-183	13C-BDE-209
46	2301-MP	13C12-BDE-28	13C12-BDE-47	13C12-BDE-47	13C12-BDE-99	13C12-BDE-100	13C12-BDE-153	13C12-BDE-154	13C12-BDE-183	13C12-BDE-209
49	2301-MP	4'-Fluoro-2,3',4,6-TetraBDE (F-BDE-069)	4'-Fluoro-2,3',4,6-TetraBDE (F-BDE-069)	4'-Fluoro-2,3',4,6-TetraBDE (F-BDE-069)	3-Fluoro-2,2',4,4',5,5'-EsaBDE (F-BDE-153)	3-Fluoro-2,2',4,4',5,5'-EsaBDE (F-BDE-153)	3-Fluoro-2,2',4,4',5,5'-EsaBDE (F-BDE-153)	3-Fluoro-2,2',4,4',5,5'-EsaBDE (F-BDE-153)	3-Fluoro-2,2',4,4',5,5'-EsaBDE (F-BDE-153)	4'-Fluoro-2,2',3,3',4,5,5',6,6'-NonaBDE (F-BDE-208)
51	2301-MP	13C12-TriBDE 28	13C12-TetraBDE 47	13C12-TetraBDE 47	13C12-PentaBDE 99	13C12-PentaBDE 99	13C12-HexaBDE153	13C12-HexaBDE153	13C12-HeptaBDE 183	13C12-DecaBDE 209
55	2301-MP	13C-BDE28	13C-BDE47	13C-BDE47	13C-BDE99	13C-BDE100	13C-BDE153	13C-BDE164	13C-BDE183	13C-BDE209
58	2301-MP									
60	2301-MP	13C-BDE153	13C-BDE153	13C-BDE153	13C-BDE153	13C-BDE153	13C-BDE153	13C-BDE153	13C-BDE153	
63	2301-MP	13C12-PBDE 28	13C12-PBDE 47	-	13C12-PBDE 99	13C12-PBDE 100	13C12-PBDE 153	13C12-PBDE 154	13C12-PBDE 183	-
64	2301-MP	BDE 28 C13	BDE 47 C13		BDE 99 C13	BDE 100 C13	BDE 153 C13	BDE 154 C13	BDE 183 C13	BDE 28 C13
76	2301-MP	C13-BDE-28	C13-BDE-47		C13-BDE-99	C13-BDE-100	C13-BDE-153	C13-BDE-154	C13-BDE-183	C13-BDE-209
77	2301-MP	C13-PBDE-28	C13-PBDE-47	C13-PBDE-47	C13-PBDE-99	C13-PBDE-99	C13-PBDE-153	C13-PBDE-154	C13-PBDE-183	
78	2301-MP	13C12 BDE 28	13C12 BDE 47	13C12 BDE 47	13C12 BDE 99	13C12 BDE 100	13C12 BDE 153	13C12 BDE 154	13C12 BDE 183	13C12 BDE 209
83	2301-MP	BDE-28	BDE-47	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	
88	2301-MP	13C BDE28	13C BDE47	13C BDE47	13C BDE99	13C BDE100	13C BDE153	13C BDE154	13C BDE183	13C BDE209
96	2301-MP	13C BDE-28	13C BDE-47	13C BDE-47	13C BDE-99	13C BDE-100	13C BDE-153	13C BDE-154	13C BDE-183	13C BDE-209
98	2301-MP	BDE-28	BDE-47	BDE47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	BDE-209
101	2301-MP	13C BDE 28	13C BDE 47		13C BDE 99	13C BDE 100	13C BDE 153	13C BDE 154	13C BDE 183	13C BDE 209
115	2301-MP	BDE-28-13C12	BDE-47-13C12	BDE-47-13C12	BDE-99-13C12	BDE-100-13C12	BDE-153-13C12	BDE-154-13C12	BDE-183-13C12	BDE-209-13C12
121	2301-MP	BDE 28 13C12	BDE 47 13C12		BDE 99 13C12	BDE 100 13C12	BDE 153 13C12	BDE 154 13C12	BDE 183 13C12	
125	2301-MP	13C12-TriBDE 28	13C12-TetraBDE 47	13C12-TetraBDE 47	13C12-PentaBDE 99	13C12-PentaBDE 99	13C12-HexaBDE153	13C12-HexaBDE153	13C12-HeptaBDE 183	13C12-DecaBDE 209
126	2301-MP	BDE-28L	BDE-47L		BDE-99L	BDE-100L	BDE-153L	BDE-154L	BDE-183L	BDE-209L

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Methods PBDEs - Recovery Standards

LC	Sample	BDE 28	BDE 47	BDE 49	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209
2	2301-MP	79	79	79	79	79	139	139	180	206
3	2301-MP									
9	2301-MP	13C BDE-77	13C BDE-77	13C BDE-77	13C BDE-77	13C BDE-77	13C BDE-138	13C BDE-138	13C BDE-138	13C BDE-138
11	2301-MP	BDE-79	BDE-79	BDE-79	BDE-79	BDE-79	BDE-138	BDE-138	BDE-138	BDE-206
12	2301-MP									
14	2301-MP	13C-BDE-118	13C-BDE-118	13C-BDE-118	13C-BDE-118	13C-BDE-118	13C-BDE-118	13C-BDE-118	13C-BDE-208	13C-BDE-208
18	2301-MP	13C-BDE 118	13C-BDE 118	13C-BDE 118	13C-BDE 118	13C-BDE 118	13C-BDE 118	13C-BDE 118	13C-BDE 118	13C-BDE 118
19	2301-MP	L-BDE-79 (13C)	L-BDE-79 (13C)	L-BDE-79 (13C)	L-BDE-139 (13C)	L-BDE-139 (13C)	L-BDE-139 (13C)	L-BDE-139 (13C)	L-BDE-139 (13C)	L-BDE-206 (13C)
27	2301-MP	13C-BDE-139	13C-BDE-139	13C-BDE-139	13C-BDE-139	13C-BDE-139	13C-BDE-139	13C-BDE-139	13C-BDE-139	13C-BDE-139
31	2301-MP									
34	2301-MP	13C-BDE-79	13C-BDE-79	13C-BDE-79	13C-BDE-138	13C-BDE-138	13C-BDE-138	13C-BDE-138	13C-BDE-138	13C-BDE-206
37	2301-MP	13C-BDE-77	13C-BDE-77	13C-BDE-77	13C-BDE-126	13C-BDE-126	13C-BDE-126	13C-BDE-126	13C-BDE-126	13C-BDE-207
46	2301-MP	13C12-BDE-139	13C12-BDE-139	13C12-BDE-139	13C12-BDE-139	13C12-BDE-139	13C12-BDE-139	13C12-BDE-139	13C12-BDE-139	13C12-BDE-139
49	2301-MP	2'-Fluoro-2,4,4'-TriBDE (F-BDE-028)	2'-Fluoro-2,4,4'-TriBDE (F-BDE-028)	2'-Fluoro-2,4,4'-TriBDE (F-BDE-028)	5-Fluoro-2,2',3,4,4',5',6-EptaBDE (F-BDE-183)	5-Fluoro-2,2',3,4,4',5',6-EptaBDE (F-BDE-183)	5-Fluoro-2,2',3,4,4',5',6-EptaBDE (F-BDE-183)	5-Fluoro-2,2',3,4,4',5',6-EptaBDE (F-BDE-183)	5-Fluoro-2,2',3,4,4',5',6-EptaBDE (F-BDE-183)	5-Fluoro-2,2',3,4,4',5',6-EptaBDE (F-BDE-183)
51	2301-MP	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138
55	2301-MP	13C-BDE126	13C-BDE126	13C-BDE126	13C-BDE126	13C-BDE126	13C-BDE126	13C-BDE126	13C-BDE126	13C-BDE126
58	2301-MP									
60	2301-MP									
63	2301-MP	13C12-PCB 52	13C12-PCB 52	-	13C12-PCB 138	13C12-PCB 138	13C12-PCB 138	13C12-PCB 138	13C12-PCB 138	-
64	2301-MP	PCB 138	PCB 138		PCB 138	PCB 138	PCB 138	PCB 138	PCB 138	PCB 138
76	2301-MP	C13-BDE-139	C13-BDE-139		C13-BDE-139	C13-BDE-139	C13-BDE-139	C13-BDE-139	C13-BDE-139	C13-BDE-139
77	2301-MP	C13-PCB-80	C13-PCB-80	C13-PCB-80	C13-PCB-80	C13-PCB-80	C13-PCB-80	C13-PCB-80	C13-PCB-80	
78	2301-MP	13C12 BDE 139	13C12 BDE 139	13C12 BDE 139	13C12 BDE 139	13C12 BDE 139	13C12 BDE 139	13C12 BDE 139	13C12 BDE 139	13C12 BDE 139
83	2301-MP	BDE-77	BDE-77	BDE-77	BDE-77	BDE-77	BDE-138	BDE-138	BDE-138	
88	2301-MP	13C BDE139	13C BDE139	13C BDE139	13C BDE139	13C BDE139	13C BDE139	13C BDE139	13C BDE139	13C BDE139
96	2301-MP	13C BDE-77	13C BDE-77	13C BDE-77	13C BDE-77	13C BDE-77	13C BDE-138	13C BDE-138	13C BDE-138	
98	2301-MP	PCB-138	PCB-138	PCB-138	PCB-138	PCB-138	PCB-138	PCB-138	PCB-138	PCB-138
101	2301-MP	13C BDE 77	13C BDE 77		13C BDE 77	13C BDE 77	13C BDE 138	13C BDE 138	13C BDE 138	13C BDE 238
115	2301-MP	BDE-77-13C12	BDE-77-13C12	BDE-77-13C12	BDE-77-13C12	BDE-77-13C12	BDE-138-13C12	BDE-138-13C12	BDE-138-13C12	BDE-138-13C12
121	2301-MP	PCB 170 13C12	PCB 170 13C12		PCB 170 13C12	PCB 170 13C12	PCB 170 13C12	PCB 170 13C12	PCB 170 13C12	
125	2301-MP	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138	13C12-HexaBDE138
126	2301-MP	BDE-139L	BDE-139L		BDE-139L	BDE-139L	BDE-139L	BDE-139L	BDE-139L	BDE-139L

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Methods PBDEs - Comments

LC	Sample		BDE 28	BDE 47	BDE 49	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209
2	2301-MP										<3 x blank native level
3	2301-MP										
9	2301-MP										
11	2301-MP										
12	2301-MP				not analyzed, not included in the scope						
14	2301-MP										
18	2301-MP										
19	2301-MP										
27	2301-MP										
31	2301-MP										
34	2301-MP										
37	2301-MP										
46	2301-MP										
49	2301-MP										
51	2301-MP										
55	2301-MP		136% IS recovery	130% IS recovery	130% IS recovery	118% IS recovery	94% IS recovery	54% IS recovery	67% IS recovery	127% IS recovery	39% IS recovery
58	2301-MP										
60	2301-MP										not analysed
63	2301-MP				not analysed						not analysed
64	2301-MP		Internal Standard-EO 5275	Recovery Standard-EO 5277	Cambridge isotope						
76	2301-MP				Not included						After subtraction of background
77	2301-MP										
78	2301-MP										
83	2301-MP										
88	2301-MP										
96	2301-MP										
98	2301-MP										
101	2301-MP										
115	2301-MP										
121	2301-MP				N/A						N/A
125	2301-MP										
126	2301-MP				not determined						

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Physico-chemical Methods HBCDDs - Internal standards

LC	Sample	Weighed sample [g]	Use of isotope-labelled internal standards for … HBCDD diastereomers (yes/no)
2	2301-MP		
3	2301-MP	5	yes
9	2301-MP		
11	2301-MP	20	yes
12	2301-MP		
14	2301-MP	10.6	yes
18	2301-MP	1	yes
19	2301-MP	10	yes
27	2301-MP	2.5	yes
31	2301-MP	9.725	Yes
34	2301-MP	50	yes
37	2301-MP		
46	2301-MP	15	yes
49	2301-MP		
51	2301-MP	5	yes
55	2301-MP	28.39	yes
58	2301-MP	8	yes
60	2301-MP		
63	2301-MP	5	yes
64	2301-MP		
76	2301-MP		
77	2301-MP		
78	2301-MP	10.2	yes
88	2301-MP		
96	2301-MP	3	YES
98	2301-MP	30	yes
101	2301-MP	10	yes
115	2301-MP	2	yes
121	2301-MP		
125	2301-MP	5	yes
126	2301-MP		

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Methods HBCDDs - Internal Standards

LC	Sample		(+/–)-α-HBCDD	(+/–)-β- HBCDD	(+/–)-γ- HBCDD
2	2301-MP				
3	2301-MP		M-aHBCDD	M-bHBCDD	M-gHBCDD
9	2301-MP				
11	2301-MP		alpha-HBCDD	beta-HBCDD	gamma-HBCDD
12	2301-MP				
14	2301-MP		13C-alfa-HBCD	13C-beta-HBCD	13C-gamma-HBCD
18	2301-MP		alpha-HBCDD-C13	beta-HBCDD-C13	gamma-HBCDD-C13
19	2301-MP		13C12-aHBCDD	13C12-bHBCDD	13C12-gHBCDD
27	2301-MP				
31	2301-MP		13C A-HBCD	13C B-HBCD	13C Y-HBCD
34	2301-MP		13C-α-HBCD	13C-β-HBCD	13C-γ-HBCD
37	2301-MP				
46	2301-MP		13C alphaHBCDD	13C betaHBCDD	13C gammaHBCDD
49	2301-MP				
51	2301-MP		13C12-α-HBCD	13C12-β-HBCD	13C12-γ-HBCD
55	2301-MP		13C-a-HBCD	13C-B-HBCD	13C-j-HBCD
58	2301-MP		13C alpha-HBCDD	13C beta-HBCDD	13C gamma-HBCDD
60	2301-MP				
63	2301-MP		alfa-HBCDD (13C12)	beta-HBCDD (13C12)	gamma-HBCDD (13C12)
64	2301-MP				
76	2301-MP				
77	2301-MP				
78	2301-MP		13C12 alfa-HBCDD	13C12 beta-HBCDD	13C12 gamma-HBCDD
88	2301-MP				
96	2301-MP		13C-α-HBCDD	13C-β-HBCDD	13C-γ-HBCDD
98	2301-MP				
101	2301-MP		13C-alpha-HBCD	13C-gamma-HBCD	13C-gamma-HBCD
115	2301-MP		alfa-HBCD-13C12	gamma-HBCD-13C12	gamma-HBCD-13C12
121	2301-MP				
125	2301-MP		13C12-α-HBCD	13C12-β-HBCD	13C12-γ-HBCD
126	2301-MP				

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Methods HBCDDs - Recovery Standards

LC	Sample		(+/–)-α-HBCDD	(+/–)-β- HBCDD	(+/–)-γ- HBCDD
2	2301-MP				
3	2301-MP		18D-bHBCDD	18D-bHBCDD	18D-bHBCDD
9	2301-MP				
11	2301-MP		D18-beta-HBCDD	D18-beta-HBCDD	D18-beta-HBCDD
12	2301-MP				
14	2301-MP		d18-alpha-HBCD	d18-beta-HBCD	d18-gamma-HBCD
18	2301-MP		alpha-HBCDD-d18	beta-HBCDD-d18	gamma-HBCDD-d18
19	2301-MP		aHBCDD-d18	bHBCDD-d18	gHBCDD-d18
27	2301-MP				
31	2301-MP		D18-B-HBCD	D18-B-HBCD	D18-B-HBCD
34	2301-MP		13C-δ-HBCD	13C-δ-HBCD	13C-δ-HBCD
37	2301-MP				
46	2301-MP		d18-racbeta-1,2,5,6,9,10 - Hexabromocyklododecane	d18-racbeta-1,2,5,6,9,10 - Hexabromocyklododecane	d18-racbeta-1,2,5,6,9,10 - Hexabromocyklododecane
49	2301-MP				
51	2301-MP		d18-β-HBCD	d18-β-HBCD	d18-β-HBCD
55	2301-MP		none	none	none
58	2301-MP				
60	2301-MP				
63	2301-MP				
64	2301-MP				
76	2301-MP				
77	2301-MP				
78	2301-MP				
88	2301-MP				
96	2301-MP		d18-β-HBCDD	d18-β-HBCDD	d18-β-HBCDD
98	2301-MP				
101	2301-MP				
115	2301-MP		beta-HBCD-13C12	beta-HBCD-13C12	beta-HBCD-13C12
121	2301-MP				
125	2301-MP		d18-β-HBCD	d18-β-HBCD	d18-β-HBCD
126	2301-MP				

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Methods HBCDDs - Comments

LC	Sample		(+/–)-α-HBCDD	(+/–)-β- HBCDD	(+/–)-γ- HBCDD
2	2301-MP				
3	2301-MP				
9	2301-MP				
11	2301-MP				
12	2301-MP				
14	2301-MP				
18	2301-MP				
19	2301-MP				
27	2301-MP				
31	2301-MP			<LOQ	<LOQ
34	2301-MP				
37	2301-MP				
46	2301-MP				
49	2301-MP				
51	2301-MP				
55	2301-MP		108% IS recovery	106% IS recovery	104% IS recovery
58	2301-MP				
60	2301-MP				
63	2301-MP				
64	2301-MP				
76	2301-MP				
77	2301-MP				
78	2301-MP				
88	2301-MP				
96	2301-MP				
98	2301-MP				
101	2301-MP				
115	2301-MP				
121	2301-MP				
125	2301-MP				
126	2301-MP				

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for Halogenated Persistent Organic Pollutants (POPs) in Feed and Food
11 March 2024

Annex 7: Overview participants' methods – Extractions, clean-up and detection

Test sample - Milk Powder (2301-MP)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Physico-chemical Methods PBDEs - Pre-treatment and extraction

LC	Sample		**Pre-treatment and extraction** Sample preparation/pre-treatment	Extraction technique	Extraction solvent	Extraction time [h]	Extraction temperature [ºC]	Extraction pressure [MPa]
2	2301-MP		No sample pre-treatment, used directly from container supplied.	Hydrochloric acid digestion	3:1 (v/v) Hexane: Dichloromethane	12h	ambient	ambient
3	2301-MP							
9	2301-MP		Milk reconstitution in MilliQ water with Ultraturrax	Liquid-Liquid	Röse-Gottlieb protocol			
11	2301-MP		reconstitution of liquid milk by adding water	solvent partitioning (liquid-liquid extraction)	ethanol/diethylether/petroleum ether (1/2/2)			
12	2301-MP		no	manually liquid-liquid extraction	n-hexane:acetone 1/1			
14	2301-MP		water addition	L-L extraction	dichloromethane-hexane		ambient	ambient
18	2301-MP		solved with hot water and lyophilized; LLE of Toluene 3x with water after Soxhlet, drying with Na2SO4 before further sample preparation	Soxhlet	Toluene/Ethanol 30/70	40		
19	2301-MP			ASE	Ethanol/Toluene (7/3)	15 min	100 °C	10
27	2301-MP		Reconstitution of test ssample in hot water with addition of ammonia	Liquid-liquid extraction	diethyl ether and petroleum ether			
31	2301-MP							
34	2301-MP		Homogenisation	Soxhlet	Toluene /ethanol 50 / 50	24	120	atm
37	2301-MP			Twisselman	Toluene / Ethanol (30/70)	6		
46	2301-MP		freeze-dried	Accelerated Solvent Extraction (ASE)	dichloromethane/hexane/methamol (25/60/15)	22 min	100	10
49	2301-MP		no	ASE	toluene	0,75	140	10,342
51	2301-MP		homogenization, drying with polyacrylamide	cold extraction	hexane		room temperature	
55	2301-MP		treatment as milk (1.34 g powder + 9 g water)	LLE	PE - Acetone			
58	2301-MP		reconstitution with water	LLE mit oxalic acid /Petroleum ehter/n-pentane				
60	2301-MP		resolve in water	liquid/liquid	diethylether/hexane 1/1		roomtemperature	ambient
63	2301-MP		thorough homogenization, powder reconstitution with MQ water (1:9), acid hydrolysis (sodium oxalate,ethanol)	(ultrasonic bath, agitate), L-L cold extraction (2 fold)	diethylether, n-hexane	2	20	0.1
64	2301-MP		no	ASE	Toluene:Cyclohexane	40min	130oC	1500
76	2301-MP			Shaking on robot	Water/Ethyl acetate 1:1	0,25	40	10
77	2301-MP			Soxhlet	DCM	18	Boiling	
78	2301-MP		drying	UAE	DCM:hexane (1:1)	1	40	room
83	2301-MP		the sample of milk powder was reconstituted with water	Liquid-Liquid partition	1) add Ethanol/amonia -turrax 5 min, 2) add Diethyl Ether turrax 5 min, 3) add Petroleum Ether turrax 5 min			
88	2301-MP		no	ASE	Toluen:Ethanol (90:10)	1	100	10,342
96	2301-MP		drying	PLE	Toluene/Acetone			
98	2301-MP		Homogenisation	ASE, LLE	ASE: hexane : 2-propanol (3:2, v/v), LLE: ethanol : DEE : n-hexane (10 : 4 : 6, v/v/v), n-hexane	ASE: 30 min/sample, LLE: 30 min/sample	ASE: 120°C, LLE: ambient temperature	ASE: 10MPa, LLE: atmospheric pressure
101	2301-MP		mixing	PSE	DCM:n-hexane:MeOH (45:45:10)	3 cycles per 2 minutes	65°C	10 MPa
115	2301-MP		no	QuEChERs like-extraction	Ethyl acetate	no	no	no
121	2301-MP			ASE	HEXANE/ACETONE 50/50	0.33	100	10.13
125	2301-MP		homogenization, drying with polyacrylamide	cold extraction	hexane		room temperature	
126	2301-MP		no	Buechi Speed Extractor	Ethanol/Toluene 70/30	2 x 0,1	100	10

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Physico-chemical Methods PBDEs - Clean-up

LC	Sample		Clean-up Gelchromatography	Silica/sulfuric acid column	Florisil column	Alumina column	Carbon column	Others	Final volume [µl]: PBDE
2	2301-MP		No	Yes	No	Yes	Yes	Sample extract partitioned with concentrated sulfuric acid to remove bulk organic material residues	10µL
3	2301-MP								
9	2301-MP		no	yes	no	yes	yes		100
11	2301-MP		no	yes	no	yes	no	acid hydrolysis with sulphuric acid	40
12	2301-MP		no	no	no	no	no	sulfuric acid treatment, silica gel column	100 ul
14	2301-MP		no	yes	no	yes	yes	no	500
18	2301-MP		no	yes	no	yes	yes	Silica/AgNO3	100
19	2301-MP		no	yes	no	yes	yes	AgNO3 (MIURA)	50
27	2301-MP		Yes	Yes	Yes	No	Yes	No	50
31	2301-MP								
34	2301-MP		no	yes	no	yes	no		25
37	2301-MP		no	yes	no	yes	no	acidic treatment	50
46	2301-MP		no	yes	yes	yes	no	no	50
49	2301-MP		no	yes	no	yes	no	no	50
51	2301-MP		no	yes	no	yes	no		100
55	2301-MP		no	yes	no	no	no		250
58	2301-MP		no	yes	no	yes	yes		100
60	2301-MP		no	yes	no	yes	yes	no	200 µL
63	2301-MP		no	yes	no	yes	yes	basic silica, silver nitrate silica	30
64	2301-MP			yes		yes	yes		100
76	2301-MP		no	yes	no	yes	yes	Silver nitrate column	1000
77	2301-MP		No	Yes	No	Yes	Yes	-	50
78	2301-MP		yes	yes	no	no	yes		20
83	2301-MP		no	yes	no			basic set of "power-prep system" columns	40
88	2301-MP		no	yes	no	yes	no		200
96	2301-MP		YES	YES	YES	NO	YES		50
98	2301-MP		no	yes	yes	yes	yes	PowerPrep FMS columns (basic-neutral silica, alumina, carbon)	20
101	2301-MP		no	yes	no	no	yes	no	no
115	2301-MP		yes	no	no	no	no	Extrelut NT-3 column, acidic for H2SO4 tandem Si 1g/6 mL column	250
121	2301-MP		NO	YES	YES	NO	YES	NO	100
125	2301-MP		no	yes	no	yes	no		100
126	2301-MP		no	yes	no	yes	yes		30

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Physico-chemical Methods PBDEs - Chromatographic separation and detection method

LC	Sample		Chromatographic separation and detection method			
			GC injection	Injected volume [µl]	Chromatographic separation: Stationary phase	Detector
2	2301-MP		PTV	1µL	5%-Phenyl-Arylene-95% DimethylPolysiloxane (ZB5-MS) column 30m×0.1mm×0.1µm	Thermo DFS HRMS (>10,000 Mass resolution)
3	2301-MP					
9	2301-MP		PTV	5	RTX-1614 (15x0.25x0.10)	HRMS
11	2301-MP		PTV	2	Rtx-1614 30m x 0.25mm x 0.1µm	HRMS
12	2301-MP		NCI	6	DB-5MS, 15 m x 0,25 mm id, 0,10 um	LRMS
14	2301-MP		splitless	5	(5%-phenyl)-methylpolysiloxane	MSMS
18	2301-MP		PTV	1	ZB - Semi Volatiles, 20m, 0.18 mm, 0.18µm	MS/MS
19	2301-MP		large volume	6	Rtx-1614 (15m x 0,25 mm x 0,1 µm) + 1,5m retention gap	MS/MS
27	2301-MP		PTV	1	Rtx-1614 (30 m x 0.25 mm x 0.1 um)	Autospec Premier HRMS (SIR)
31	2301-MP					
34	2301-MP		splitless	1	Rtx-1614	HRMS
37	2301-MP		splitless	2.0	DB-5HT	HRMS (Autospec Ultima Waters)
46	2301-MP		PTV Splitless	1	60m DB-5ms; 15 m RTX 1614	HRMS
49	2301-MP		MMI	3	DB5	GC-MS/MS-NCI
51	2301-MP		pulsed splitless	2	Diphenyl-/dimethylpolysiloxan (5%/95%)	MS/MS
55	2301-MP		PTV	10	RTX-CL-pesticides	HRMS
58	2301-MP		splitless	2	HP-5MS (Agilent) 25 m, 0.11 □m film thickness, 0.20 mm ID	HRMS
60	2301-MP		MMI	2 µL	DB-XLB	MS/MS
63	2301-MP		pulsed splitless	1	DB-5MS (60m x 0,25mm x 0,10 µm)	HRMS (R>10000)
64	2301-MP		Splitless	2	DB 5 MS, 30m, 0.25mm, 0.25um	MS/MS
76	2301-MP		PTV	2	DB5-MS	HRMS
77	2301-MP		Splitless	1.0	DB-5MS	HRMS, DFS
78	2301-MP		PTV	5	Phenomenex Zebron ZB-Semivolatiles	
83	2301-MP		Splitless	1	DB-5MS (30 m, 0.25 mm id, 0,25 mm film)	HRMS (Mat-95 XP)
88	2301-MP		splitless	2	%5 phenyl %95 polydimethylsiloxane	APGC-MS/MS
96	2301-MP		Splitless	2	HT8PCB	GC-HRMS
98	2301-MP		splitless	2	DB-5ht (30m x 0,25mm x 0,1um)	HRMS
101	2301-MP		pulsed splitless	2	RTX-1614	HRMS
115	2301-MP		PTV	10	DB5HT 15 m x 0.25 mm; 0.1 um	MS/MS
121	2301-MP		Splitless	1	100% dimethylpolysiloxane	LRMS/MS
125	2301-MP		pulsed splitless	2	Diphenyl-/dimethylpolysiloxan (5%/95%)	MS/MS
126	2301-MP		PTV	1	Rtx-1614	HRMS

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Physico-chemical Methods HBCDDs - Pre-treatment and extraction

LC	Sample	**Pre-treatment and extraction** Sample preparation/pre-treatment	Extraction technique	Extraction solvent	Extraction time [h]	Extraction temperature [ºC]	Extraction pressure [MPa]
2	2301-MP						
3	2301-MP			hexane:dichloromethane 50/50	0.33	ambiente	ambiente
9	2301-MP						
11	2301-MP	reconstitution of liquid milk by adding wate	liquid-liquid partitioning process	ethanol/diethylether/petroleum ether (1/2/2)			
12	2301-MP						
14	2301-MP	water addition	L-L extraction	dichloromethane-hexane		ambient	ambient
18	2301-MP		Soxhlet	Toluene	12	unknown	ambient pressure
19	2301-MP	cold extraction	DCM/Hexan 1/1	roughly 2-3 hours	ambient	ambient	
27	2301-MP						
31	2301-MP	None	ASE	Hexane:Acetone 50:50	0.5	100	10.3
34	2301-MP	Homogenisation	Soxhlet	Toluene /ethanol 50 / 50	24	120	atm
37	2301-MP						
46	2301-MP	no	ASE 350	dichloromethane/hexane/methamol (50/50)	0.3	120	10
49	2301-MP						
51	2301-MP	homogenization	Quechers	acetonitrile/water (1/1)	10 min	room temperature	
55	2301-MP	treatment as milk (1.34 g powder + 9 g water)	LLE	PE - acetone			
58	2301-MP	reconstitution with water	LLE mit oxalic acid /Petroleum ehter/n-pentane				
60	2301-MP						
63	2301-MP	drying	shaking with dichlormethan : acetone 2:1 for 90 min	100 ml of dichlormethan : acetone 2:1	90 min	ambient	0.10
64	2301-MP						
76	2301-MP						
77	2301-MP						
78	2301-MP	drying	UAE	DCM:hexane (1:1)	1	40	room
88	2301-MP						
96	2301-MP	drying	PLE	Toluene/Acetone			
98	2301-MP	Homogenisation	ASE, LLE	ASE: hexane : 2-propanol (3:2; v/v), LLE: ethanol : DEE : n-hexane (10 : 4 : 6, v/v/v), n	ASE: 30 min/sample, LLE: 30 min/sample	ASE: 120°C, LLE: ambient temperature	ASE: 10MPa, LLE: atmospheric pressure
101	2301-MP	mixing	PSE	DCM:n-hexane:MeOH (45:45:10)	3 cycles per 2 minutes	65°C	10 MPa
115	2301-MP		QuEChERS-like	Ethyl Acetate			
121	2301-MP						
125	2301-MP	homogenization	Quechers	acetonitrile/water (1/1)	10 min	room temperature	
126	2301-MP						

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Physico-chemical Methods HBCDDs - Clean-up

LC	Sample		**Clean-up** Gelchromatography	Silica/sulfuric acid column	Florisil column	Alumina column	Carbon column	Others	Final volume [µl]: HBCDD
2	2301-MP								
3	2301-MP		no	yes	no	no	no		200
9	2301-MP								
11	2301-MP		no	yes	no	no	no	acid hydrolysis with sulphuric acid	100
12	2301-MP								
14	2301-MP		no	yes	no	yes	yes	no	500
18	2301-MP		no	yes	yes	no	no	no	500
19	2301-MP		no	yes	no	no	no	no	400
27	2301-MP		No	Yes	Yes	No	No	No	50
31	2301-MP		No	Yes	Yes	No	No	None	100
34	2301-MP		no	yes	no	no	no		1000
37	2301-MP								
46	2301-MP		no	yes	no	no	no		20
49	2301-MP								
51	2301-MP		no	yes	no	no	no		1000
55	2301-MP		no	yes	no	no	no	no	500
58	2301-MP		yes	no	no	no	no	silica gel column	500
60	2301-MP								
63	2301-MP		yes	yes	no	no	no		500
64	2301-MP								
76	2301-MP								
77	2301-MP								
78	2301-MP		yes	yes	no	no	yes		200
88	2301-MP								
96	2301-MP		YES	YES	NO	NO	NO	liquid liquid extraction	50
98	2301-MP		no	yes	no	no	no	elution of Silica/sulfuric acid column after elution of PCDD/Fs, PCBs with DCM in n-hexane (10% and 50%)	10
101	2301-MP		no	yes	no	no	no	no	50
115	2301-MP		yes	no	no	no	no	Extrelut NT-3 column, acidic for H2SO4 tandem Si 1g/6 mL column	250
121	2301-MP								
125	2301-MP		no	yes	no	no	no		1000
126	2301-MP								

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Physico-chemical Methods HBCDDs - Chromatographic separation and detection method

		Chromatographic separation and detection method			
LC	Sample	Injection	Injected volume [µl]	Chromatographic separation: Stationary phase	Detector
2	2301-MP				
3	2301-MP	UPLC	5	Eclipse Plus C18, 2,1 x 100mm	MS/MS
9	2301-MP				
11	2301-MP		5	BEH C18 (50 mm x 2.1 mm; 1.7 µm)	HRMS
12	2301-MP				
14	2301-MP	syringe	5	C18	MS/MS
18	2301-MP	direct injection	5, 10, 20, 40	reversed phase C18 (Eclipse XDB-C18 5µm 4,6x150mm)	MS/MS
19	2301-MP		15	C18	MS/MS
27	2301-MP	HPLC	5	C18	Orbitrap-HRMS
31	2301-MP		10	C18	HRMS (hybrid quadrupole/orbitrap)
34	2301-MP	LC		Acquity BEH C18 150 mm	MS/MS
37	2301-MP				
46	2301-MP		10	Hypersil Gold C18, 100x2,1mm, 1,9µm)	LC-MS/MS
49	2301-MP				
51	2301-MP	standard	10	C18	MS/MS
55	2301-MP	LC-injection	10	C18	LC-MSMS
58	2301-MP		10	RP 18	LC-MS/MS
60	2301-MP				
63	2301-MP	normal	10	C18	MS/MS
64	2301-MP				
76	2301-MP				
77	2301-MP				
78	2301-MP		70	Luna PHP	MS/MS
88	2301-MP				
96	2301-MP		15	Hypersil Gold	MS/MS
98	2301-MP	splitless	2	DB-5ht (30m x 0,25mm x 0,1um)	HRMS
101	2301-MP	LC	5	C-18	MS/MS
115	2301-MP		20 µL	KINETEX 2.6um XB-C18 100A (100 x 2.1 mm) (PHENOMENEX)	LC-MS/MS
121	2301-MP				
125	2301-MP	standard	10	C18	MS/MS
126	2301-MP				

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for Halogenated Persistent Organic Pollutants (POPs) in Feed and Food
11 March 2024

Annex 8: Overview participants' methods – Measurement uncertainty and Limit of Quantification

Test sample - Milk Powder (2301-MP)

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Determination of Limit of Detection and Measurement Uncertainty (MU) - PBDEs

LC	Sample	Methods apllied to determine Limit of Quantification (LOQ)	Measurement Uncertainty (MU)	Additional Information
2	2301-MP			Calculation methodology as per USEPA Method 1614
3	2301-MP			
9	2301-MP	LOQs have been determined by the procedural blank approach and the signal to noise approach	Measurment uncertainty have been calculated based on spiked samples results within the method validation	PBDEs have been analysed in the PCBs fraction of the dioxin protocol
11	2301-MP	The LOQs were estimated using the approach "Congener-based LOQs from S/N Calculations". This methodology is reported in the Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food.	The MU was estimated using the "semi-empirical approach" based on the ISO Guide to the expression of Uncertainty in Measurement applied to analytical chemistry by EURACHEM/CITAC. This approach is reported in the Guidance Document on Measurement Uncertanty for performing PCDD/F and PCB Analysis using Isotope Dilution Mass SpectrometryLaboratories	
12	2301-MP	standarddeviation of the blanks multiplied with a factor of 6	MU was calculated by the root of the sum of the measurement uncertainty for reproducibility and recovery including bias. Expanded uncertainty is then calculated by multiplying MU with a factor of 2	the expanded uncertainty for total HBCDD is 55 % and the IS used is 13C-BDE-155
14	2301-MP		Calculated from precision (control sample) and bias (PTs), expanded uncertainty. However, MU calculation based on sample concentrations higher than in this PT . Until now, MU calculated for only sum PBDE parameter	
18	2301-MP	blank + 3s		
19	2301-MP			One set of data was extracted using ASE (see obove), another set was extracted using cold exrtraction with cyclohexane/DCM (1/1), ambient conditions. The reported contents are average values of both methods. The lipid content was determined using denaturation with acetone/water (4/1) followed by soxleth extraction (hexane/DCM/ethanol, 5/2/1). In addition the Weibull-Stoldt method was used to determine the lipid content and a value of 9,4 % was received.
27	2301-MP			
31	2301-MP			
34	2301-MP			
37	2301-MP			
46	2301-MP	LOQ was obtained from blank samples made in the same batch as PT samples.	Obtained during method validation additional, MUs were compared with a standard deviation of PT sample, higher value was taken to report.	
49	2301-MP		For the estimation of uncertainty, in addition to the precision of the method, the uncertainty components linked to systematic effects on mass and volume measurements, the calibration curve, the curve point control and recovery were assessed.We used th metrological approach	
51	2301-MP			
55	2301-MP	validation; reporting limit	validation	
58	2301-MP	according to regulation 2017/644	according Guidance Document on Measurement Uncertainty for Laboratories performing PCDD/F and PCB Analysis using Isotope Dilution Mass Spectrometry“	
60	2301-MP			
63	2301-MP			
64	2301-MP			
76	2301-MP	Calculated by the TargetQuan software		
77	2301-MP			
78	2301-MP	lowest spiked level meeting criteria fro inter-day precision (RSD 20%) and trueness (70-130%)	MU was calculated on the basis of fortification experiments, by summing contributions of errors from reproducibility and deviation from theoretical (spiked) value	
83	2301-MP			
88	2301-MP			
96	2301-MP	S/N > 3		
98	2301-MP	LOQ = 3 x LOD; LOD evaluated as 3 times of noise	Expanded U: Ue = k x Uc (k = 2). MU of type A is evaluated using internal RM. U of type B (includes i.a. uncertainity of weighing, volume measurements, etc.) Uc = combined uncertainty is summed uncertainty of type A and B according the law of propagation of measurement uncertainty	
101	2301-MP			
115	2301-MP	Samples spiked at LOQ level (5 pg/g; 100ppg for BDE 209); for BDE 47 LOQ (15 pg/g) was estimated from procedural blanks run within the sample batch	Nordtest	
121	2301-MP			
125	2301-MP			
126	2301-MP	LOQ of each individual congener is determined by TargetQuan and has the factors 3 for noise and 2 for sigma.	MU is calculated from the standard deviation of the repetition in the laboratory and that of the interlaboratory comparison and is valid for relevant contents	

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Methods PBDEs - Limit of detection (LOQ) in µg/kg wet weight

LC	Sample	BDE 28	BDE 47	BDE 49	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209
2	2301-MP	0.0012	0.0075	0.0003	0.0024	0.0001	0.0001	0.0003	0.0001	0.3
3	2301-MP									
9	2301-MP									
11	2301-MP	0.00049	0.034	0.00098	0.014	0.0049	0.00029	0.00052	0.00012	0.031
12	2301-MP	0.005								
14	2301-MP									
18	2301-MP	0.0021	0.029	0.00087	0.012	0.003	0.00043	0.0034	0.0039	0.18
19	2301-MP									
27	2301-MP	0.003	0.002	0.003	0.008	0.007	0.006	0.003	0.004	0.007
31	2301-MP									
34	2301-MP									
37	2301-MP									
46	2301-MP	0.0007	0.0006	0.0008	0.0017	0.0011	0.0014	0.0013	0.0022	0.0124
49	2301-MP			0.01						
51	2301-MP	0.002	0.002	0.002	0.004	0.004	0.006	0.006	0.01	0.2
55	2301-MP	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.035
58	2301-MP									
60	2301-MP	0.002								
63	2301-MP									
64	2301-MP	1								10
76	2301-MP	0.001	0.001		0.0008	0.007	0.0008	0.0007	0.002	0.0035
77	2301-MP	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	
78	2301-MP	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
83	2301-MP	0.00001	0.00002	0.00002	0.00004	0.00004	0.00003	0.00003	0.00008	
88	2301-MP	0.002072	0.000512	0.000469	0.000415	0.000369	0.000341	0.000268	0.000516	0.001801
96	2301-MP									
98	2301-MP	0.000146904	5.93881E-05	5.93881E-05	0.000477222	0.000292439	0.000259477	0.000153956	0.000365103	0.024925433
101	2301-MP	0.000041	0.000098		0.00623	0.0151	0.000264	0.000094	0.000211	0.00102
115	2301-MP	0.005								
121	2301-MP									
125	2301-MP	0.002	0.002	0.002	0.004	0.004	0.006	0.006	0.01	0.2
126	2301-MP	0.00012	0.00018		0.00023	0.00029	0.00019	0.00017	0.00021	0.00068

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Methods PBDEs - Measurement Uncertainty [%]

LC	Sample	BDE 28	BDE 47	BDE 49	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209
2	2301-MP	±15	±15	±15	±15	±15	±15	±15	±15	
3	2301-MP									
9	2301-MP	27.3	28	25.2	27.5	24.9	23.4	28	21.4	21.7
11	2301-MP	28	41	34	34	27	27	28	36	40
12	2301-MP	40	40		40	30	30	30	40	50
14	2301-MP	70	30	70	30	30	30	50	50	50
18	2301-MP	30	30	30	30	30	30	30	30	40
19	2301-MP									
27	2301-MP									
31	2301-MP									
34	2301-MP									
37	2301-MP	30	30	60	30	30	30	30	30	30
46	2301-MP	22	19.2	15.1	15.2	12.1	23.5	19.5	21.7	28.6
49	2301-MP	60	39	67	41	40	50	60	42	40
51	2301-MP	30	30	30	30	30	30	30	30	30
55	2301-MP	25	25	25	25	25	30	25	25	50
58	2301-MP									
60	2301-MP									
63	2301-MP	30	30	-	30	30	30	30	30	-
64	2301-MP	25	25		25	25	25	25	25	25
76	2301-MP	30								
77	2301-MP	10	10	10	10	10	10	10	10	
78	2301-MP	35	25	45	30	30	25	30	25	45
83	2301-MP									
88	2301-MP	37.97	33.97		44.66	36.87	44.69	33.28	37.24	47.62
96	2301-MP									
98	2301-MP	64.5	20.4	20.4	17.6	19.7	19.95	23.7	9.68	31.4
101	2301-MP	15.3	12.9		12	17.2	18.9	16	21.2	16.5
115	2301-MP		42	59	42	59	59	59	59	42
121	2301-MP									
125	2301-MP	30	30	30	30	30	30	30	30	30
126	2301-MP	25	25		25	25	25	25	25	25

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]
EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)
Determination of Limit of Detection and Measurement Uncertainty (MU) - HBCDDs

LC	Sample		**Methods apllied to determine** Limit of Quantification (LOQ)	Measurement Uncertainty (MU)	Additional Information
2	2301-MP				
3	2301-MP		no experience with this matrix	U= k*u=((2x CVrw) + biais)	
9	2301-MP				
11	2301-MP		The LOQ was estimated following the "Calibration Standards" approach. This methodology is reported in the Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food.	The MU was estimated using the Top-Down approach reported in the Guidance Document on Measurement Uncertanty for Laboratories performing PCDD/F and PCB Analysis using Isotope Dilution Mass Spectrometry	
12	2301-MP				
14	2301-MP		Combination of low level spike and blank results.	Combination of low level spike and PT results.	
18	2301-MP		calculated on base of standard with S/N 10:1 multiplied with the worst recovery rate	estimated value based on the RSD of multiple determination	Method according to Bichon et.al. 2018
19	2301-MP		ten point equidistant calibration in matrix at the expected LOQ using DIN 32645		The lipid content was determined using denaturation with acetone/water (4/1) followed by soxleth extraction (hexane/DCM/ethanol, 5/2/1). In addition the Weibull-Stoldt method was used to determine the lipid content and a value of 9,4 % was received.
27	2301-MP				
31	2301-MP		Lowest validated level	Not yet assessed, validation in progress	
34	2301-MP				
37	2301-MP				
46	2301-MP		Lowest calibration level		
49	2301-MP				
51	2301-MP				
55	2301-MP		validation	validation	
58	2301-MP		lowest calibration point		
60	2301-MP				
63	2301-MP				
64	2301-MP				
76	2301-MP				
77	2301-MP				
78	2301-MP		lowest spiked level meeting criteria for inter-lab precision (RSD 20%) and trueness (70-130%)	MU was calculated on the basis of fortification experiments, by summing contributions of errors from reproducibility error and deviation from theoretical (spiked) value	
88	2301-MP				
96	2301-MP				
98	2301-MP		LOQ = 3 x LOD LOD evaluated as 3 times of noise	Expanded U: Ue = k x Uc (k = 2). MU of type A is evaluated using internal RM. U of type B (includes i.a. uncertainity of weighing, volume measurements, etc.) Uc = combined uncertainty is summed uncertainty of type A and B according the law of propagation of measurement uncertainty	
101	2301-MP				
115	2301-MP		Samples spiked at LOQ level (10 pg/g) within the batch	Nordtest	
121	2301-MP				
125	2301-MP				
126	2301-MP				

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Methods HBCDDs - Limit of detection (LOQ) in µg/kg wet weight

LC	Sample		(+/–)-α-HBCDD	(+/–)-β- HBCDD	(+/–)-γ- HBCDD
2	2301-MP				
3	2301-MP		0.04	0.02	0.04
9	2301-MP				
11	2301-MP		0.005	0.005	0.005
12	2301-MP				
14	2301-MP		0.1	0.1	0.1
18	2301-MP		0.06	0.06	0.06
19	2301-MP				0.01
27	2301-MP		0.01	0.01	0.01
31	2301-MP		0.03	0.03	0.03
34	2301-MP				0.01
37	2301-MP				
46	2301-MP		0.005	0.005	0.005
49	2301-MP				
51	2301-MP		0.006	0.006	0.006
55	2301-MP		0.048	0.01	0.032
58	2301-MP				0.005
60	2301-MP				
63	2301-MP		0.05	0.05	0.05
64	2301-MP				
76	2301-MP				
77	2301-MP				
78	2301-MP		0.01	0.01	0.01
88	2301-MP				
96	2301-MP				
98	2301-MP				
101	2301-MP		0.0025	0.0035	0.00175
115	2301-MP			0.01	0.01
121	2301-MP				
125	2301-MP		0.006	0.006	0.006
126	2301-MP				

EURL Proficiency Test on the Determination of PCDD/Fs, PCBs, PBDEs, HBCDDs and PFASs in Milk Powder 2023 [EURL-PT-POP_2301-MP]

EURL for halogenated Persistent Organic Pollutants (POPs) in Feed and Food

Milk Powder (2301-MP)

Methods HBCDDs - Measurement Uncertainty [%]

LC	Sample		(+/–)-α-HBCDD	(+/–)-β- HBCDD	(+/–)-γ- HBCDD
2	2301-MP				
3	2301-MP		50	50	50
9	2301-MP				
11	2301-MP		27	30	32
12	2301-MP				
14	2301-MP		30	30	30
18	2301-MP		30	30	30
19	2301-MP				
27	2301-MP				
31	2301-MP				
34	2301-MP				
37	2301-MP				
46	2301-MP				
49	2301-MP				
51	2301-MP		30	30	30
55	2301-MP		13	7.5	13
58	2301-MP		25	25	25
60	2301-MP				
63	2301-MP		23	18	16
64	2301-MP				
76	2301-MP				
77	2301-MP				
78	2301-MP		30	30	30
88	2301-MP				
96	2301-MP				
98	2301-MP				
101	2301-MP		9	17	5
115	2301-MP		36	49	49
121	2301-MP				
125	2301-MP		30	30	30
126	2301-MP				